Lucie Jade Johnson

Finding radiogenic Sr-isotope biospheres: can a home in Britain be found for people with high $^{87}Sr/^{86}Sr$?

Abstract: With increasing regularity archaeological humans with $^{87}Sr/^{86}Sr$ >0.714 are being excavated in Britain and are difficult to explain or identify possible places of origin. The main aim of this thesis was to identify any geological or anthropological reasons for their high $^{87}Sr/^{86}Sr$ values. Therefore, plant $^{87}Sr/^{86}Sr$ data has been obtained from several Precambrian lithologies and igneous intrusions in Britain with the aim of identifying values >0.714. Only 20 of the 151 samples measured recorded values >0.714. It was found that biosphere $^{87}Sr/^{86}Sr$ values >0.714 represented only 10% of all known British Sr-isotope biosphere data and only ~2.8% of the area of Britain. They are thus numerically and spatially rare and can also be considered agriculturally marginal for archaeological populations.

Unexpectedly, plant samples collected from ancient woodlands were found to have elevated values by +0.002 compared to plant samples collected from unforested land on the sedimentary Triassic bedrock of central England. Further work is needed to replicate this result and to establish if the same trend is found on other bedrock lithologies. This finding could have major implications for how biosphere and human $^{87}Sr/^{86}Sr$ data are interpreted in archaeological migration and mobility studies, particularly in recently de-forested regions.

Three British quern or millstone rock types (Millstone Grit, Pennant Sandstone and granite) were investigated to establish if they could contribute bioaccessible high $^{87}Sr/^{86}Sr$ directly in the human stomach from rock grit accidently ingested via grinding grain, or deliberately through pica or geophagy, using the Unified Bioaccessiblity Method (UBM: Hamilton *et al.,* 2015). The results showed that Sr in ingested rock grit is bioaccessible to humans. However, unrealistic quantities of rock grit needs to be consumed to significantly alter skeletal $^{87}Sr/^{86}Sr$ (e.g. to change the value by ±0.001 or greater). The study thus provides reassurance that non-local or unusually high $^{87}Sr/^{86}Sr$ values cannot be explained by the direct ingestion of rock grit, clays or soils.

Finding radiogenic Sr-isotope biospheres: can a home in Britain be found for people with high $^{87}Sr/^{86}Sr$?

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Table of Contents

List of Tables

Chapter 2

Chapter 3

Chapter 4

Chapter 7

Chapter 8

List of Figures

All the Figures within this thesis are listed below, but only including the first line of their descriptions.

Separate Figures

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

Chapter 7

Chapter 8

Declaration

The study investigating the bioaccessibility of Sr within rock grit, using the Unified Bioaccessibility Method, in chapter 7 of this thesis was a collaborative project funded through NIGSFC grant No.IP-1456-0514 awarded to Janet Montgomery. I, Lucie Johnson, collected all the samples, prepared and processed them and wrote several drafts of what will form a co-authored paper. Elliot Hamilton provided guidance and assistance during the Unified Bioaccessibility Method, Jane Evans provided guidance and assistance during the Sr-isotope analysis, while both Janet Montgomery and Jane Evans helped write and provided constructive comments during the formation of what will be a co-authored paper.

Acknowledgements

What a strange experience of misery and joy producing this thesis has been. Thank you to the department of Archaeology, at Durham University for awarding me the NERC doctoral studentship (Award Reference No.1345819) to complete this thesis and my deepest gratitude goes towards my supervisors Janet Montgomery and Jane Evans, who's advice, comments, critics and continued encouragement have guided me through its creation. Both Janet and Jane have been, and are amazing! For all the meetings, coffee and cake or lunch outings and the endless reading of drafts, thank you Janet and Jane. Hopefully I have not caused you both too much stress.

During my visits to the NIGL (BGS, Keyworth, Nottinghamshire) everyone I have met has been friendly and incredibly helpful. Particularly thanks goes towards: Jane Evans and Carlyn Stewart, for their guidance and assistance through the chemical preparation of my plant samples for Sr-isotope analysis, until I was confident to proceed alone and also for preparing and running all the samples on the Thermo Triton multi-collector mass spectrometer; Adrian Wood, for his assistance during preparing the rocks in the Mineral Separation Laboratory facility, I really enjoyed listening to rock music while crushing rocks; Elliot Hamilton, for his guidance and assistance of the Unified Bioaccessibility Method. A special thanks also goes towards the late Professor David Peacock, a leading authority and author of 'The Stone of Life. Querns, Mills and Flour Production in Europe up to c.AD 500', whose advice and interest was greatly appreciated in the early stages of the UBM study.

I have had various help with my fieldwork along the way too. Firstly, Janet spent a lot of time with me, going over several geological maps while I decided where to sample. Then Jane Evans accompanied and taught me the logistics of collecting plant samples during the sampling of Charnwood Forest and also drove me to the Forest of Dean and back, to collect a couple of brick-sized samples of Pennant Sandstone. During my trip to the Malvern Hills I was accompanied by my younger brother, Ryan, and he was bloody useless! All he did was eat my food, complain about my driving and laugh when I fell in a ditch of stinging nettles. At least his terrible singing was mildly entertaining. To my other half, Adam, I am very grateful to you for driving me around and going on long walks into the wilderness in the Cairngorms National Park, Scotland, driving me there and back again, in one day, to collect some slabs of Eskdale Granite from the Lake District in the pouring rain and finally taking me on another excursion around the Lake District to collect plant samples, this time though it was gloriously sunny.

For answering questions, providing information or where to find it and generally showing interest in work, thank goes towards Ben Roberts, Mike Church, Andrew Millard, Peter Rowley-Conwy, Penny Wilson and Mike White in the Department of Archaeology, Durham University. In particular Ben Roberts, Mike White and Penny Wilson were part of my review panel through the four years of study and so their feedback and guidance, as non-specialist in isotope analysis, has been very useful. To my fellow postgraduates and friends, Abi Molenaar (formally Taylor, she got married this year, so exciting), Floor Huisman, Lisa Snape-Kennedy and Edward Caswell, thank you for your support and help with all thing archaeological or, in Ed's case, all things to do with arcGIS. To Abi and Floor in particular, thanks for all the cake and trips out too that keep a person sane.

To my family, thank you for listening and supporting me. I know it has not always been easy to understood what I do or how I do it (my mum tells people and do science 'stuff' with leaves), but thank you for trying, or at least pretending not to be bored. Finally, to Adam, again, you have been my chauffeur, my IT specialist and my punching bag when I could not handle my emotions too well. Let me clarify, I did not actually punch him, even though he may of preferred a punch over my grumpiness, it's just a turn of phrase. Thank you for dealing with my excel tantrums and generally being the adult in our relationship during the finally few months of writing up this thesis. I swear that I'll start tidying up after myself, helping with the chores and providing you with undying attention now that I'm done (you probably know only one of these statements will be true, guess which?). Overall, just a big, massive thank you to anyone and everyone who helped me in anyway, it has and will always be appreciated!

1. Introduction

Sr-isotopes ($^{87}Sr/^{86}Sr$) are a valuable tool for archaeologists to investigate human and animal migration and mobility. To provide context for the skeletal $^{87}Sr/^{86}Sr$ data, information is also needed about the $^{87}Sr/^{86}Sr$ available in the environment, often referred to as the biosphere. Proxies for the Sr-isotope biosphere tend to include modern soil, water, plant samples as well as modern or archaeological bone/dentine samples (Price *et al.,* 2002; Bentley, 2006; Montgomery, 2010; Evans *et al.,* 2010). Plants are particularly important because they are the dominant dietary input of Sr in animals and humans (Burton & Wright, 1995; Montgomery, 2010). A preliminary Sr-isotope biosphere map of Britain has been produced (Figure 1.1: Evans *et al.*, 2010) and there have been further additions to the Sr-isotope biosphere data in Britain, such as a recent doctorate which characterised in detail chalk biospheres in southern England (Warham, 2011, University of Bradford). This is still very much a work in progress, with further preparations being taken to produce an interactive multi-isotope map of Britain by Evans *et al.* (in prep; Evans, *pers.com*.).

The majority of archaeological humans with $^{87}Sr/^{86}Sr$ data available in Britain, are excavated from regions where bone preservation is good, such as from chalk, limestone and sedimentary bedrocks. The chalk and limestone bedrocks in Britain typically produce biosphere $^{87}Sr/^{86}Sr$ between 0.707 - 0.710, while sedimentary silicate bedrock can range in value from 0.709 - 0.713, depending on the age and lithologies of the bedrock (Figure 1.1: Evans *et al.,* 2010). A review of all the published $^{87}Sr/^{86}Sr$ data for archaeological humans excavated in Britain was produced by Evans *et al.* (2012). Their study included 614 archaeological humans, with a mean $^{87}Sr/^{86}Sr = 0.7099 \pm 0.0026$ (2SD), the majority of which are consistent with the current biosphere $^{87}Sr/^{86}Sr$ values available in Britain. Only a handful of archaeological humans in Britain recorded $^{87}Sr/^{86}Sr > 0.714$ (Evans *et al.*, 2012) and, apart from on the granitic regions of Scandinavia (Åberg *et al.,* 1998; Sjögren *et al.,* 2009; Sjögren & Price, 2013; Price *et al.,* 2017), the same is true across most of Europe, where one or two people with $^{87}Sr/^{86}Sr > 0.714$ may be found in a published study. These people in Britain are often referred to as having radiogenic $^{87}Sr/^{86}Sr$, meaning they have high values >0.714, and because of a lack of understanding of high Sr-isotope biospheres, they are simplistically assigned as either non-British or originating from upland or granitic regions (see Jay *et al.,* 2007; Evans *et al.,* 2012).

However, with increasing regularity archaeological humans with $^{87}Sr/^{86}Sr$ >0.714 are being excavated in Britain dating to the Neolithic, Bronze Age and Iron Age. The main locations or areas where these people have been excavated in Britain can be seen in Figure 1.2. It has been difficult to explain or identify possible places of origin for these people in Britain, even when using other isotope data (e.g. $\delta^{18}O$‰) in conjunction with their $^{87}Sr/^{86}Sr$ data (Parker Pearson *et al.* 2016; Neil *et al.,* 2017; Waddington *et al.* in press). Such values are also starting to become more common in domesticated animals, such as cattle (Jay *et al.,* 2007; Montgomery *et al.,* unpublished report). There are only a few places in Britain that record biosphere $^{87}Sr/^{86}Sr$ >0.714 and they are mainly in Scotland. Geologically, Scotland consists of mainly very old bedrocks (Precambrian to late Palaeozoic) as well as rocks of a granitic nature, and these have produced biosphere $^{87}Sr/^{86}Sr$ >0.714 and on rare occasions >0.720 (e.g. hotspots in Evans *et al.,* 2010). The Sr-isotope biosphere data collected in Evans *et al.* (2010) was limited at the time of creation and resulted in non-systematic coverage of Britain. This means that Scotland currently does not have as much biosphere data available compared to England and Wales and the maximum biosphere $^{87}Sr/^{86}Sr$ is not well defined.

The main problem with migration from Scotland is that it is believed to be counter-intuitive in much of prehistory, when migration routes are traditionally conceived as coming from the south and east of England. However, many archaeologists are debating the importance of coastal movement and the role of rivers. Travelling across the Britain could be achieved by following the coast between estuaries or offshore islands eliminating the need to venture far into open water or using the extensive rivers that provide access into mainland Britain (Bradley, 2007, p.16-17: Cunliffe, 2013, p.67-72). Therefore England and Wales have an accessible connection to Scotland through their shared coastline. This does not rule out migration from the European continent as many significant parts of the European coastline are within 100-200km of Britain suggesting potential connections with one another. The North Sea is considered an exception for a large part of prehistory, cutting Britain off from Scandinavia, but even those areas could be linked by following the shoreline by way of Belgium and the Netherlands (Bradley, 2007, p17: Cunliffe, 2013, p.65-66) and by 8th century AD, with the onset of Viking raids, North Sea routes were actively used, such as the crossing from Norway to the Shetland Islands then to Orkney and onwards to mainland Scotland (Cunliffe, 2013, p.65-66, 459-462). Although identifying specific routes of migration into Britain is still difficult, the main burial locations or areas of the archaeological humans with high $^{87}Sr/^{86}Sr$ in Britain (Figure 1.2) are all either near to a coast or can be accessed through travelling up a major river, such as the River Trent for the Peak District or the River Wye or Severn for those found along the Wales Border.

Recent aDNA data studying the migration and movement of prehistoric people in Britain strongly suggests the importance of major population migration from outside of the Britain. Olalde *et al.* (2018) provide extensive research into genome-wide data from 400 Neolithic, Copper Age and Bronze Age Europeans, including 226 individuals associated with Beaker-complex artefacts. Through the authors interpretations they deduced that migration played a key role in the dissemination of the Beaker complex in Britain. The aDNA data of Neolithic, Copper and Bronze Age individuals, including Beaker-complex-associated individuals, identified how the spread of the Beaker complex introduced high levels of steppe-related ancestry and was associated with the replacement of approximately 90% of Britain's gene pool within a few hundred years. Isotope data used to study migration and mobility, such as oxygen and strontium isotope data, are only sensitive to first-generation migrants and $^{87}Sr/^{86}Sr$ in particular cannot differentiate between areas with similar geologies. This means it is difficult to identify substantial mobility over individuals' lifetimes from locations with cooler climates or from places with geologies typical of Britain. If no areas in Britain can be identified has having a dominant biosphere $^{87}Sr/^{86}Sr$ >0.714 then it could be acceptable to suggest that these archaeological humans excavated in Britain with $^{87}Sr/^{86}Sr$ >0.714 are first-generation migrants originating from outside of Britain.

All the archaeological humans excavated in Britain with $^{87}Sr/^{86}Sr$ >0.714 are migrants to region they are buried in, which are geological regions more conducive to bone preservation, such as the chalk, limestone and some silicate sedimentary rocks. Skeletal remains rarely survive in granitic soils and so there are no in-situ comparative populations currently available in Britain. Without in-situ populations it is difficult to define the range of $^{87}Sr/^{86}Sr$ that a granite-dwelling population should have. Furthermore, even though granites can have whole-rock $^{87}Sr/^{86}Sr$ >1.0 (Faure & Powell, 1972; Rundle, 1979; Peterman & Hildreth, 1978; Faure, 1986), this does not necessarily mean such values will be available in the biosphere, as it depends on what minerals within the granite are weathered out and hence what $^{87}Sr/^{86}Sr$ values are released.

To complicate the situation further, in Britain many of the granitic regions are at elevations and latitudes that ensure poor, wet, acidic soils that would seem unattractive for agriculture and therefore unable to sustain large populations. The high amount of rainfall (~0.7092:Veizer, 1989, p.142) that occurs on the western coast and at high altitudes in Britain (Met Office, Rainfall amount Annual Average, 1981-2010) can also dominate the Sr in soils and strongly influence the $^{87}Sr/^{86}Sr$ of plants and animals (Evans *et al.,* 2010; Montgomery *et al*., 2014). For granitic bedrocks, this results in biosphere $^{87}Sr/^{86}Sr$ that range greatly in value (0.709 to >0.714), making it even harder to obtain high values >0.714 in humans and animals (Montgomery *et al*., 2014).

A lot of focus has been put towards finding geological or environmental reasons for humans and animals excavated in Britain with high $^{87}Sr/^{86}Sr$ >0.714. However, there are certain aspects of human behaviour not currently taken into account during interpretations of skeletal $^{87}Sr/^{86}Sr$. Can high $^{87}Sr/^{86}Sr$ be obtained by unusual dietary practices that by-pass the normal transfer of strontium in the food-chain? The ingestion of soil or rock grit in humans can occur accidentally, through the use of querns and millstones, or deliberately through pica or geophagy (Eshed *et al.*, 2006; Deter, 2009). As of present, no study has directly investigated the bioaccessibility of Sr from rock grit or soil when directly ingested by a human, which could drastically change the way $^{87}Sr/^{86}Sr$ data are interpreted.

1.1 Research Questions and Objectives

Through the collection of plants, and other samples where necessary, this thesis investigates the Sr-isotope biospheres of several study areas from across Britain, to see if a home can be found for the increasing number of archaeological humans with high $^{87}Sr/^{86}Sr$ >0.714, or if such values can be obtained through unusual dietary practices. All of the study areas within this thesis can be seen in Figure 1.3.

1: Finding high $^{87}Sr/^{86}Sr$ biospheres in England and Wales?

Objectives:

a) Understand how Sr cycles through the biosphere and become familiar with the biosphere $^{87}Sr/^{86}Sr$ data currently available in Britain. Focus particularly on what causes high $^{87}Sr/^{86}Sr$ >0.714 in the biosphere *(Chapter 2).*

b) Find the areas that can potentially produce high biosphere $^{87}Sr/^{86}Sr$ within England and Wales and conduct geochemical surveys for Sr-isotope analysis *(Chapter 2 and 3).*

c) Interpret the plant $^{87}Sr/^{86}Sr$ collected from across the study areas in England *(Chapter 4).*

2: Are the high biosphere $^{87}Sr/^{86}Sr$ in Scotland reproducible, particularly values >0.720?

Objectives:

a) Become familiar with the biosphere $^{87}Sr/^{86}Sr$ data currently available in Scotland and find where biosphere $^{87}Sr/^{86}Sr$ >0.714 and >0.720 are located *(Chapter 2 and 3).*

b) Decide the most appropriate areas to collect further plant $^{87}Sr/^{86}Sr$ data in Scotland *(Chapter 3).*

c) Interpret the plant $^{87}Sr/^{86}Sr$ collected from across the study areas in Scotland *(Chapter 5).*

3: What are the maximum plant $^{87}Sr/^{86}Sr$ in Britain?

Objectives:

a) Compare and discuss plant $^{87}Sr/^{86}Sr$ data collected within this thesis with previous Sr-isotope biosphere data from England and Wales *(Chapter 4 and 8).*

b) Compare and discuss plant $^{87}Sr/^{86}Sr$ data collected within this thesis with previous Sr-isotope biosphere data from Scotland *(Chapter 5 and 8).*

c) Define the current maximum plant $^{87}Sr/^{86}Sr$ for England and Wales and Scotland, as well as the maximum $^{87}Sr/^{86}Sr$ for other proxy types where appropriate *(Chapter 8).*

<u>4: Can any other environmental reasons lead to high $^{87}Sr/^{86}Sr$ in the biospheres of Britain?</u>

Objectives:

a) Other than geological, find if any other environmental trends can cause elevated values in the biosphere from published research and reviews *(Chapter 2).*

b) Conduct a geochemical survey to test if the biospheres of ancient woodland can produce higher plant $^{87}Sr/^{86}Sr$ values than around agricultural land *(Chapter 6).*

c) During interpretation of the plant $^{87}Sr/^{86}Sr$ in this thesis, highlight any further environmental trends that have lead to values being higher than expected (*Chapter 4, 5, 6 and 7).*

d) Discuss the implications of interpreting human $^{87}Sr/^{86}Sr$ for any environmental trends that lead to higher plant $^{87}Sr/^{86}Sr$ *(Chapter 6 and 8).*

<u>5: Is the $^{87}Sr/^{86}Sr$ of rock grit ingested by humans bioaccessible and therefore can alter human $^{87}S/^{86}Sr$?</u>

Objectives:

a) Research the most common quern and millstones used in Britain, select and collect samples of three different rock types, ideally with known quarry location *(Chapter 7).*

b) Prepare three different rock samples for the Unified Bioaccessibility Method (UBM: Hamilton *et al.,* 2015) to test whether the $^{87}Sr/^{86}Sr$ in rock grit is bioaccessible to humans *(Chapter 7).*

c) Interpret the results from the UBM and discuss implications for human $^{87}Sr/^{86}Sr$ in archaeological migration and mobility studies *(Chapter 7 and 8).*

1.2 Thesis Structure

The first half of chapter 2 provides the background to strontium (Sr), Sr-isotope biospheres and the biosphere $^{87}Sr/^{86}Sr$ data currently available in Britain today (sections 2.1, 2.2 and 2.3). The second half specifically explores the geology and environmental conditions needed to produce radiogenic biospheres >0.714 along with case studies from Europe (section 2.4), before describing the possible anthropological reasons for high $^{87}Sr/^{86}Sr$ in humans (e.g. ingestion of rock grit: section 2.5). Chapter 3 outlines the pros and cons of modern biosphere proxy samples (section 3.1) resulting in plants being the main material collected, the main study areas chosen within this thesis (Figure 1.3: section 3.2.1) and the methods of collecting (geochemical surveys: section 3.2.2 and 3.2.3) and analysing plant samples for $^{87}Sr/^{86}Sr$ (section 3.3).

Chapter 4 presents all of the plant $^{87}Sr/^{86}Sr$ data from across study areas in England and Wales (excluding the Forest of Dean), with each study area following the same formatting (see table of contents). The first two study areas in chapter four were preliminary, in that they collected plant samples by slightly different methods. A single plant per analytical sample was collected from each location across Charnwood Forest (section 4.1), while multiple plants per analytical sample were collected from each location across the Malvern Hills (section 4.2). These mixed samples have been described in their respective sections, as well as in chapter 3 (section 3.2.3). All of the plant samples in the following studies of chapter 4, as well as in proceeding chapters, were collected as multiple plants per analytical sample. Chapter 5 presents all the $^{87}Sr/^{86}Sr$ data collected from across the Cairngorms National Park in Scotland.

Chapter 6 investigates whether plant samples from ancient woodlands in England can produce higher $^{87}Sr/^{86}Sr$, because of the woodland effect (chapter 2, section 2.4.3), compared to plant sample collected from around agricultural land on the same bedrock geology. Two study areas were chosen to test the woodland effect, the larger Sherwood Forest Nature Reserve, on the Triassic Sherwood Sandstone Group, and the smaller Burbage woods and common on the Triassic Mercia Mudstone Group. Chapter 7 investigates whether the rock grit of three different British quern and millstone rock types have bioaccessible $^{87}Sr/^{86}Sr$ when ingested by humans (including plant $^{87}Sr/^{86}Sr$ data from the Forest of Dean). This study is the first of its kind and employs the use of the Unified Bioaccessibility Method (UBM: Hamilton *et al.,* 2015) for Sr-isotopes.

Chapter 8 provides a discussion into the radiogenic biospheres of Britain in light of the plant $^{87}Sr/^{86}Sr$ data collected in this thesis (8.1.), defining a current maximum for the plant $^{87}Sr/^{86}Sr$ available in England and Wales and Scotland (8.1.1) and the potential of aureoles with high biosphere $^{87}Sr/^{86}Sr$ >0.714 around the base of mountains or hills (section 8.1.2). This chapter continues to discuss the implications of the newly defined maximum plant $^{87}Sr/^{86}Sr$ in Britain, on the archaeological people with high enamel $^{87}Sr/^{86}Sr$ >0.714 buried in Britain (section 8.2). Finally this chapter concludes with an unexpected section about the biosphere $^{87}Sr/^{86}Sr$ data on Triassic bedrock and how its biosphere $^{87}Sr/^{86}Sr$ can potentially be split based on the different Triassic Basins (section 8.3).

Chapter 9 concludes this thesis by revisiting the main research questions and objectives, providing advice to archaeologists wanting to collect biosphere proxy samples for their migration and mobility studies in Britain and further research needed. All statistical analysis in this thesis are reported as the mean (arithmetic), along with the standard deviation (SD), which is reported to 2SD, unless referenced from another published study. The mean was chosen as the best way to display the plant $^{87}Sr/^{86}Sr$, and biosphere $^{87}Sr/^{86}Sr$ data overall, in this thesis. The sampling of plants, and other biosphere proxies, on several bedrock lithologies in Britain has been bias and collected unevenly (Evans *et al.,* 2010). This thesis is no exception, and so the statistical use of the median or mode on plant $^{87}Sr/^{86}Sr$ collected on certain lithologies, such as granite or sandstone, masks the heterogeneous nature of their biosphere $^{87}Sr/^{86}Sr$, which is deemed unfavourable as the main aim of this thesis is to find the highest $^{87}Sr/^{86}Sr$ values possible in Britain.

The majority of the Figures in this thesis were created using GIS data that was publically available, including the BGS 1:625000 Bedrock and Superficial geology maps (DiGMapGB, 2007 and 1977), glacial geomorphological evidence of the last glaciation in Britain from BRITICE (Clark *et al*., 2004; 2017) and the Ancient Woodland Inventories for England (Natural England, 2013) and Wales (AWI, Wales, 2011). Underneath the bedrock geology data of every map, is ordnance survey DTM terrain 50 data, which displays a 50m gridded digital terrain model (*Contains OS data © Crown copyright and database right, 2017).* The bedrock geology data has been set at 40% transparency so the shades of the

DTM terrain 50 data can be seen: dark shades represent low elevations and light shades represent higher elevations.

As the bedrock geology in most of the study areas is complex and to allow for larger images of the maps themselves, a separate A2 legend has been created, referred to as Figure X, to use alongside any of the Figures containing bedrock geology in this thesis, with the exception of any that display the whole of Britain. The bedrock geology of Britain can be viewed and interacted with on the BGS website: http://www.bgs.ac.uk/discoveringGeology/geologyOfBritain/viewer.html . Figure Xi also exists separately and displays all of the biosphere $^{87}Sr/^{86}Sr$ data in this thesis, including the data from chapter 4, 5, 6 and 7 and outlines the values >0.714 in Britain. The biosphere $^{87}Sr/^{86}Sr$ data comes from Spiro *et al.* (2001), Montgomery *et al.* (2006), Trickett (2007), Leach *et al. (*2009), Montgomery *et al. (*2009), Evans *et al.* (2009), Evans *et al.* (2010), Chenery *et al.* (2010), Boulton (2011), Chenery *et al.* (2011), Warham (2011), Hemer *et al.* (2014), Neil *et al.* (2017), Evans (unpublished results; *pers.com*.), NIGL (unpublished) and this thesis.

1.Figures

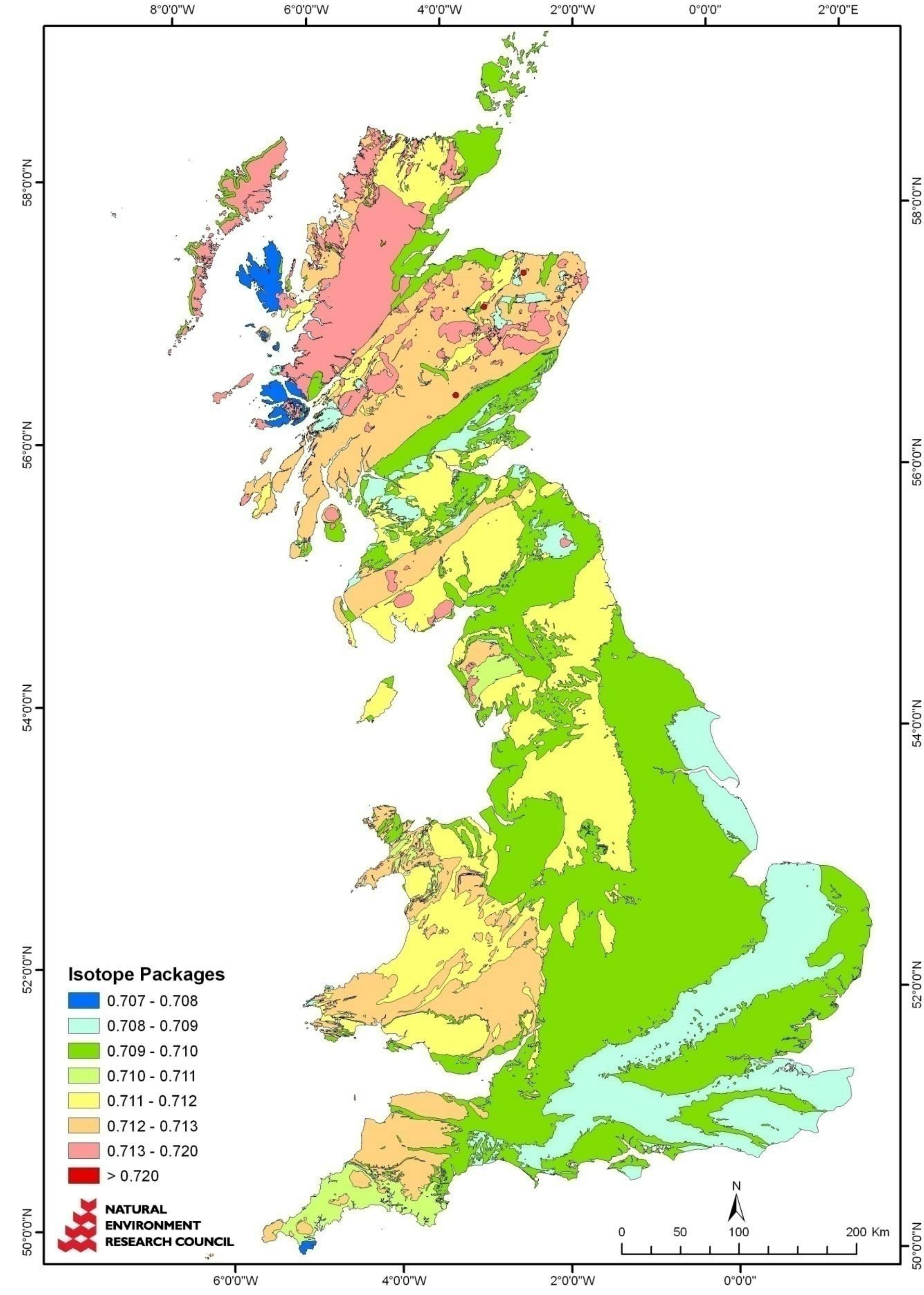


Figure 1.1. The preliminary Sr-isotope biosphere map of Britain from Evans *et al.* (2010).

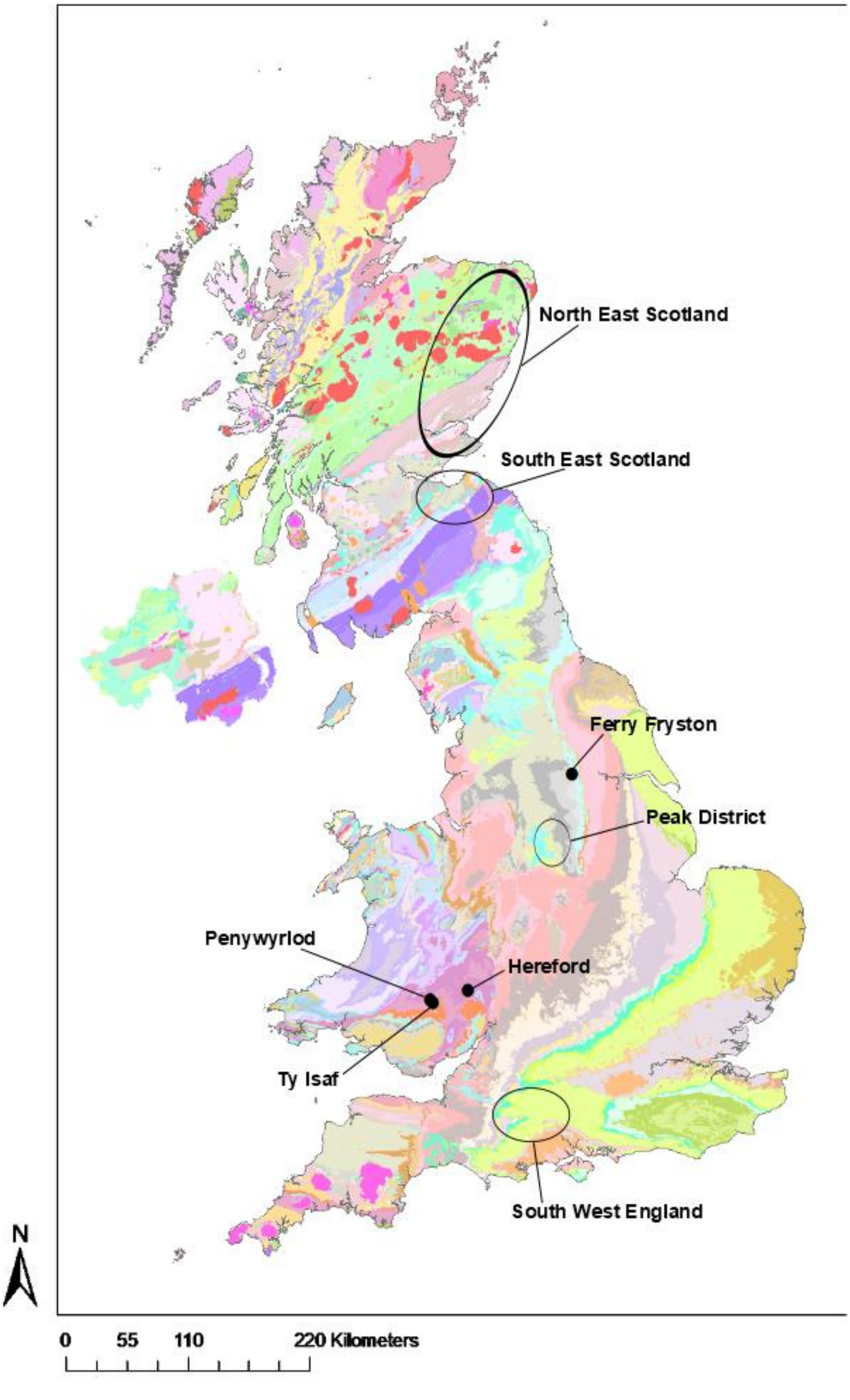


Figure 1.2. The main burial locations or areas of the archaeological humans with $^{87}Sr/^{86}Sr$ >0.714 in Britain (Jay *et al.*, 2007; Evans *et al.* 2012; Parker Pearson *et al.* 2016; Neil *et al.,* 2017). The background of Britain is based the 1:625000 BGS Bedrock geology map (DiGMapGB, 2007).

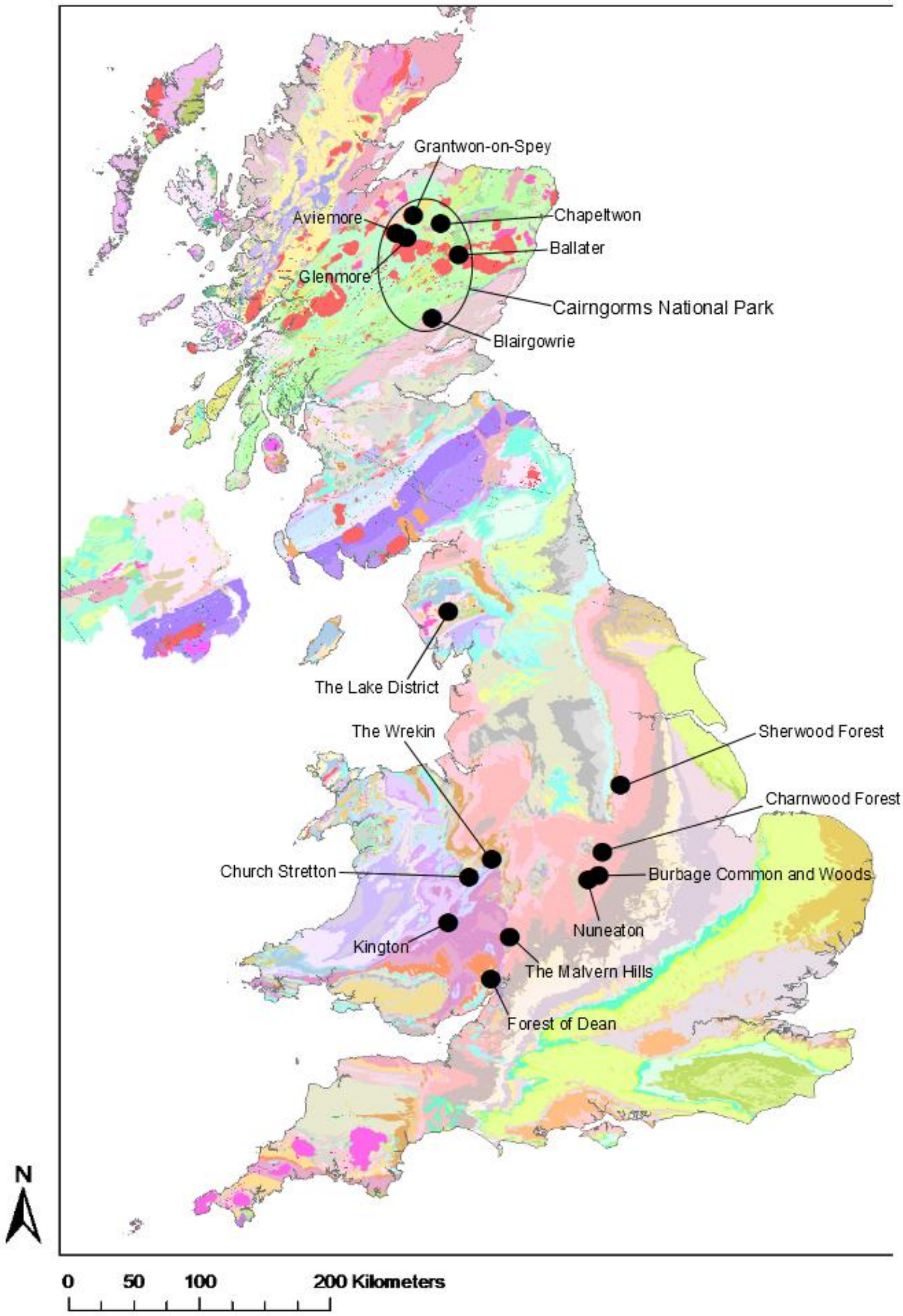


Figure 1.3. All of the study areas within this thesis, alongside the 1:625000 BGS Bedrock geology map of Britain (DiGMapGB, 2007). Study areas in chapter 4 include: Charnwood Forest (section 4.1); the Malvern Hills (section 4.2); Nuneaton (section 4.3); Church Stretton (4.4); the Wrekin (section 4.5); Kington (the Stanner-Hanter Complex, section 4.6); the Lake District (section 4.7). Study areas in chapter 5 include those within the Cairngorms, specifically a transect from Blairgowrie to Grantown-on-Spey, the area around Chapeltown and the area between Aviemore and Glenmore. Sherwood Forest and Burbage Common and Woods are in chapter 6 and the Forest of Dean study area is in chapter 7.

2. The Strontium Chapter: defining a radiogenic $^{87}Sr/^{86}Sr$ biosphere.

This chapter provides an overview into Sr-isotopes (section 2.1), how they cycle through the biosphere (section 2.2), the biosphere $^{87}Sr/^{86}Sr$ currently available in Britain (section 2.3) and how to obtain high $^{87}Sr/^{86}Sr$ values >0.714 in humans or animals, either through the bedrock into the biosphere (section 2.4) or by other potential anthropological causes (section 2.5). In brief, the more comprehensive works of Faure (1986), or the more recent and updated Faure & Mensing (2005), and Dickin (1995) are particularly useful for understanding the background chemistry of Sr, its isotopes and the evolution of radiogenic ^{87}Sr from mantle to rocks. In addition, Graustein (1989), Åberg (1995) and Capo *et al.* (1998) provide information and understanding of how Sr enters and cycles in the biosphere and how $^{87}Sr/^{86}Sr$ can be used to trace this. Price *et al*. (2002), Bentley (2006) and Montgomery (2010) also provide an overview how Sr enters and cycles in the biosphere, as well as the theoretical uses of $^{87}Sr/^{86}Sr$ for archaeologists.

2.1. Strontium (Sr) and $^{87}Sr/^{86}Sr$

Strontium, with the chemical symbol Sr, is an alkaline earth element (Group IIA) with an atomic number of 38. It is highly reactive chemically and so only occurs naturally in compounds with other elements. It is classified as a lithophile (silicate-loving), the same as its vertical neighbours in the periodic table calcium (Ca) and barium (Ba), in which Sr shares very similar physical and chemical properties. The Sr element has a valence of +2 and has an ionic radius only slightly larger than that of Ca (118pm vs. 100pm respectively; Greenwood & Earnshaw, 2005, p.111ff). This often means that Sr^{2+} can substitute Ca^{2+} in many mineral compounds, the important one from an archaeological perspective is the phosphate mineral hydroxyapatite, which is a major component of bone and tooth enamel.

Altogether Sr has four naturally occurring stable isotopes, ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr with abundances of approximately 0.56%, 9.87%, 7.04% and 82.53% respectively. The abundances of ^{84}Sr, ^{86}Sr and ^{88}Sr are constant through time. However ^{87}Sr is radiogenic and so can be produced through the β-decay of the naturally occurring radioactive isotope of Rubidium, ^{87}Rb, meaning the abundance of ^{87}Sr is ever increasing (Faure, 1986, p.117-118; Faure & Mensing, 2005, p.75-76). ^{87}Rb has a very long half-life of approximately 49 billion years (48.8Byr/4.88×10^{10} adopted by international convention; Steiger & Jager, 1977), which is considerably longer than the age of the Earth (~4.54 ± 0.05 billion years) and so any decay over archaeological time-scales is negligible. Therefore, it is known that all the ^{87}Sr in any material from the Earth has two sources: what was there when the Earth was created; the daughter material from the β-decay of ^{87}Rb. Rubidium (Rb^{+1}) can substitute for potassium (K^{+1}) in K-bearing minerals, such as silicate mica minerals and K-feldspar, due to similar ionic radii (152pm vs. 138pm respectively: Greenwood & Earnshaw, 2005, p.75ff). Because ^{87}Rb decays into ^{87}Sr, ^{87}Sr has become very useful as a geochronological and geochemical parameter in the form of a Sr-isotope ratio, $^{87}Sr/^{86}Sr$. ^{87}Sr is measured relative to ^{86}Sr as these two isotopes of Sr have similar abundances and are only one atomic mass unit apart, which reduces measurement errors (Faure, 1986, p.117-137, 154-199; Faure & Mensing, 2005, p.363-411; Bentley, 2006, p.137-141).

There are also up to 16 known unstable radioactive isotopes of Sr, ^{90}Sr and ^{89}Sr being of greatest importance in modern life. ^{90}Sr, with a half-life of approximately 30 years, is a by-product of nuclear fission found in nuclear fallout and potentially presents a health problem because of its ability to substitute calcium in the bone preventing its expulsion from the body. ^{89}Sr on the other hand is used to help with health problems. With a half-life of approximately 50.5 days, it can be created artificially and used in the treatment of bone cancer. Although these radioactive isotopes are not relevant for archaeological studies, Montgomery (2010) rightly states that because of them, more information is available on the movement of Sr through the biosphere and its uptake into the human body.

2.2. Sr-isotope biospheres

All the ^{87}Sr and ^{86}Sr which is currently in the Earth's biosphere first originated from bedrock, or specifically certain minerals within the bedrock. Over Earth's geological history different minerals within different lithologies have been weathered, primarily through chemical weathering, and have released different $^{87}Sr/^{86}Sr$ and Sr concentrations (ppm/mgkg^{-1}) into the biosphere (Faure, 1986, p.183; Capo *et al.,* 1998; Faure & Mensing, 2005, p.412-413; Bentley, 2006, p.141-143).

Once released from bedrock, Sr isotopes cycle through the soil, into groundwater, streams, rivers and lakes and the oceans (mainly via the sediments transported in rivers), into the atmosphere (precipitation and terrestrial dust) and through the food chain in plants and animals. Unlike stable isotopes commonly used for archaeological purposes (e.g. $^{18}O/^{16}O$, $^{13}C/^{12}C$, $^{15}N/^{14}N$), any fractionation that occurs during low temperature geological and biological and biochemical processes in the biosphere (including the initial weathering of the rock) are negligible when concerning $^{87}Sr/^{86}Sr$ (Graustein & Armstrong, 1983; Graustein, 1989, p.494; Miller *et al.* 1993, p.438; Capo *et al.* 1998, p.215; Blum *et al.* 2000, p.95). This is because the Sr isotopes ^{87}Sr and ^{86}Sr are heavy elements with a much lesser relative difference between their isotope masses, meaning their chemical reaction rates are depressed compared to lighter isotopes (like ^{16}O vs. ^{18}O: Hoefs, 1997, p.4-5). Overall the $^{87}Sr/^{86}Sr$ released from the bedrock remains unaltered as it cycles through the biosphere.

The biosphere $^{87}Sr/^{86}Sr$ of a given area, often referred to as the local in many archaeological studies, it is '*best expressed as a mixing system of inputs and outputs*' (Bentley, 2006, p.141). Soils, rivers and lakes (water), plants and animals tend to be intermediates in this system and so are used as proxies for the biosphere. However several terminologies are used in archaeological studies to describe these proxy samples; baseline, bioavailable and biosphere are the most common. Baseline refers to a starting point, a base for measurements and comparisons and for Sr-isotopes it refers to creating an isoscape (spatially explicit predictions of elemental isotope ratios). Baseline $^{87}Sr/^{86}Sr$ is often used for more geological applications (for example see Bataille & Bowen, 2012) and is not a term commonly used in UK and European archaeological studies. In UK archaeological studies biosphere $^{87}Sr/^{86}Sr$ is the most commonly used term, with the biosphere being the regions of the Earth's surface and atmosphere occupied by living organisms (for a few examples see Evans *et al.,* 2010; Chenery *et al.*, 2010; Montgomery, 2010). In European archaeological studies the same type of data is often termed bioavailable $^{87}Sr/^{86}Sr$, describing the value that is available for incorporation into animal and plants (for a few examples see Bentley, 2006; Maurer *et al.*, 2012; Frei & Frei, 2011; 2013; Frei & Price 2012). Although they are similar there are subtle differences between these terms and they are not always used correctly. Soil, water, plant and animal samples can all be used as proxies for the biosphere, but the $^{87}Sr/^{86}Sr$ analysed from soil and water may not necessarily pass on into the food-chain, so only plants and animals can be used to distinguish what $^{87}Sr/^{86}Sr$ values are truly bioavailable in the local environment. Because this thesis will be comparing and averaging the $^{87}Sr/^{86}Sr$ of soil, water, plant and animal samples from across Britain, the term biosphere is deemed the best way to describe them as a whole.

It is often the underlying bedrock geology that is the main contributor of $^{87}Sr/^{86}Sr$ to the biosphere (Åberg *et al.,* 1998). The $^{87}Sr/^{86}Sr$ released into the above soil and groundwater will depend on the type of lithology or lithologies (and hence minerals) being weathered. Because certain minerals are more susceptible to being weathered out of a rock, the whole-rock $^{87}Sr/^{86}Sr$ value of a bedrock lithlogy should not be used as a substitute for biosphere $^{87}Sr/^{86}Sr$. Whole-rock $^{87}Sr/^{86}Sr$ values are measurements of all the Sr-isotopes of all the minerals within a rock sample and often have much higher values compared to the biosphere $^{87}Sr/^{86}Sr$ on the same bedrock geology. Quaternary superficial deposits, consisting of unconsolidated deposits formed from around 2.6 Myr to present, are another potential geological input of Sr to the biosphere. Glacial deposits such as till, often contain debris eroded from local bedrock (<10km) but sometimes also contain larger boulders from greater distances (~100km: Kirkbride, 2002; Bradwell & Everest, 2005) and so have the potential to introduce exotic $^{87}Sr/^{86}Sr$. Other, more recent superficial deposits such as peat, can sometimes restrict the extent in which the underlying bedrock contributes $^{87}Sr/^{86}Sr$ to the biosphere and are highly absorbent shifting the biosphere towards the $^{87}Sr/^{86}Sr$ derived from atmospheric sources (Evans *et al.*, 2009).

Atmospheric sources in Britain mainly equate to precipitation (rain, snow, hail, etc.) and precipitation will get its initial $^{87}Sr/^{86}Sr$ from seawater. This marine value is an average of all the weathered components of the continental crust across the world that are deposited in the oceans (Faure, 1986, p.186-191). The Sr in the oceans has a long residence time (~2 x 10^7 years) compared to the turnover time of the oceans (millennia) and so the $^{87}Sr/^{86}Sr$ of seawater is homogenous across the world at any given time (Wadleigh *et al.,* 1985; Faure, 1986, p.186-191; Åberg, 1995, p.310; Bentley, 2006, p.146,). Through the Phanerozoic, the marine $^{87}Sr/^{86}Sr$ has ranged from around 0.707 to 0.709, but the modern day value of 0.7092 (rounded from 0.70918) is the accepted standard and remains unaltered across most archaeological time scales (Veizer, 1989, p.142; McArthur *et al.,* 2001; Faure & Mensing, 2005, p.436-447; Bentley, 2006, p.146). When in coastal areas sea-spray from the oceans will be input of marine $^{87}Sr/^{86}Sr$ (0.7092) and has the potential to dominate the coastal Sr-isotope biosphere (Montgomery *et al.,* 2003; Bentley, 2006, p.152-153; Evans *et al.,* 2009; Montgomery, 2010).

Precipitation from coastal areas will also retain marine value of 0.7092, being close to its source, however as precipitation moves further inland its $^{87}Sr/^{86}Sr$ value can change. This is because the atmosphere also contains terrestrial dust or aerosols (and also modern pollution) which are usually higher in $^{87}Sr/^{86}Sr$ value than seawater depending on its source. Terrestrial dust (etc.) can be deposited by itself, but it is often incorporated into precipitation, hence deviating the $^{87}Sr/^{86}Sr$ from the marine value (Andersson *et al.* 1990;Miller *et al.* 1993, 438; Bacon & Bain 1995, 45; Åberg, 1995,p.311; Negrel & Roy, 1998; Land *et al.* 2000, p.315; Probst *et al.,* 2000 p.209). In Britain the majority of the precipitation does not substantially deviate from the marine value of 0.7092, however there is some degree of geographic variation, with $^{87}Sr/^{86}Sr$ values changing by ±0.0005 (n=15, 2SD) at elevated, inland sites and regionally by the influence of any potential radiogenic bedrock outcrops (Warham, 2011, p.150-163). The $^{87}Sr/^{86}Sr$ value in precipitation can also show seasonal variation across the year in Britain, but the mean annual $^{87}Sr/^{86}Sr$ value remains around the marine value of 0.7092 and so is not a major concern when later interpreting $^{87}Sr/^{86}Sr$ results (Warham, 2011, p.150-163).

Modern human activities that lead to pollution of our environment, from industries to road dust to even salt grit, can alter biosphere $^{87}Sr/^{86}Sr$, particularly the $^{87}Sr/^{86}Sr$ of precipitation (Probst *et al.,* 2000; Åberg, 2001). Agricultural fertilisers can similarly contribute $^{87}Sr/^{86}Sr$ to the soil and groundwater, which can then easily be transferred to streams and rivers (Bentley, 2006, p.150-154). Fertiliser $^{87}Sr/^{86}Sr$ values vary depending on the type used, ranging from 0.703 - 0.715, although values around 0.708 -0.709 are the most common (Vitoria *et al.,* 2004). There is debate into how much fertilisers contribute to the bioavailable $^{87}Sr/^{86}Sr$ in the biosphere and therefore makes it into the food-chain. Frei & Frei (2011) calculated that modern fertilisers contribute a minimal amount, if any, to the $^{87}Sr/^{86}Sr$ of surface waters in Denmark and conclude any animals eating plants from or drinking from water sources that percolate through agricultural land applied with fertilisers would see the same negligible effect. Conversely, the more recent Sr-isotope analysis of oak cores (over 10 years sample increments) from County Antrim, Ireland, have shown that since 1947 to 1965 the $^{87}Sr/^{86}Sr$ of the oak tree based on agricultural land shifted from approximately 0.7061 to 0.7064 (Crowley *et al.*, 2015). In contrast an oak tree on a non-agricultural control site showed no such shift remaining around a value of 0.7060. Crowley *et al.,* (2015) determine that this shift in the $^{87}Sr/^{86}Sr$ of the oak tree on agricultural land was due to the application of modern fertilisers. If modern fertilisers or other pollution can change to the $^{87}Sr/^{86}Sr$ within the biosphere, a consideration needs to be made about the difference in which the value shifts and if it will be noticed within the food-chain. Usually when interpreting and discussing $^{87}Sr/^{86}Sr$ in migration and mobility studies, any change to the 4th significant figure of the ratio can be considered irrelevant: local populations can vary by 0.0002-0.002 (Evans *et al*., 2009, p.627-628), even siblings can vary by 0.0002 (Montgomery, 2002, p.146) and cattle born and raised in the same estate herd by 0.0006 (Towers, 2013, p.123-124). When considering the archaeological past, pollution and fertilisers are not considered significant contributors of $^{87}Sr/^{86}Sr$ to the local Sr biosphere (Åberg et *al.*, 1998), however it is worth pointing out that the use of lime to fertilise crops is not a modern day practice and has been recorded since the Roman period (Goulding *et al.,* 1989; Goulding, 2016).

Another important consideration of all these inputs and outputs is their Sr concentrations (ppm/mgkg^{-1}), which can make a difference to the overall biosphere $^{87}Sr/^{86}Sr$ value analysed through the different proxies (e.g. soils, rivers, plants and animals). Bentley (2006, p.140) produced a table that summarises potential Sr concentration values in natural materials and is shown in Figure 2.1 and Frei (2012, p.114) produced a useful figure which displays these values alongside Sr concentrations expected in teeth, bones and hair, which can be seen in Figure 2.2.

The underlying bedrock geology is usually the dominant contributor of $^{87}Sr/^{86}Sr$ because its Sr concentration tends to be the highest, but this all depends on the lithology (or lithologies) being weathered. Lithologies with high whole rock $^{87}Sr/^{86}Sr$, e.g. >1.0 such as granites, schists and gneisses, tend to have low Sr concentrations (Faure & Powell, 1972; Rundle, 1979; Peterman & Hildreth, 1978; Faure, 1986,p.118, 171-173). If granites, schists or gneisses are weathered alongside a carbonate rock such as chalk for example, with low $^{87}Sr/^{86}Sr$ <0.709 and often high Sr concentrations, the overlying soil will reflect the $^{87}Sr/^{86}Sr$ released from the carbonate predominately. Quaternary Superficial deposits can also sometimes dominate the bedrock geology because of their high Sr concentrations. For example, the $^{87}Sr/^{86}Sr$ from humans of the local Norse community on the Outer Hebrides show that the biosphere was dominated by the $^{87}Sr/^{86}Sr$ of the Quaternary machair over the Precambrian bedrock (being mainly Lewisian gneisses: Montgomery *et al.,* 2003). Precipitation (usually ~0.7092) tends to have very low Sr concentrations (<1.0 ppm), however in climates involving high rainfall, which causes high saturation of the soil, the $^{87}Sr/^{86}Sr$ from precipitation can dominate the local Sr-isotope biosphere and this can be seen through the $^{87}Sr/^{86}Sr$ of soils, plants and animals (Veizer, 1989; Evans *et al.,* 2010; Montgomery *et al*., 2014). The same can be said for sea-spray in coastal regions, with sea-spray often having higher Sr concentration than precipitation (Bentley, 2006, p.140). The $^{87}Sr/^{86}Sr$ from precipitation can also dominate river $^{87}Sr/^{86}Sr$ at low elevations, where mixing of tributaries vs. precipitation is prevalent due to comparable Sr concentrations. At high elevations, high weathering rates result in $^{87}Sr/^{86}Sr$ that reflects the bedrock geology, regardless of rainfall (Bentley, 2006, p.143-144).

The complex system of inputs and outputs throughout the Sr-isotope biosphere means that it is not considered good practice just to use a geological map and the whole rock $^{87}Sr/^{86}Sr$ from the bedrock, or specific mineral $^{87}Sr/^{86}Sr$ within certain bedrock lithologies, to predict the local biosphere $^{87}Sr/^{86}Sr$ (Bentley, 2006; Evans *et al.,* 2009; Evans *et al.,* 2010; Frei & Frei, 2011, 2012). Instead sampling proxies of the biosphere, usually the intermediates of the system (e.g. soils, water, plants and animals) are considered best, as they can highlight unusual values often unexplained by the underlying bedrock geology. However, a variety of Sr-isotope data can be used in simple end-member, or mixing, models to predict or separate out dominance (Faure, 1986, p.141-153; Faure, 1998; Beard & Johnson, 2000; Faure & Mensing,2005, p.347-362). The end-members can be whole rock $^{87}Sr/^{86}Sr$ values to show the assumed mixing of two lithologies, the different Sr-isotope inputs of a river, different Sr-isotope inputs in the local biosphere like rainwater vs. fertilisers or even the Sr-isotope content of different foods for animals and humans. These models can be useful both before and during interpretations of $^{87}Sr/^{86}Sr$ data.

Validation for using modern proxy data to establish biosphere values for the past has been reported in Evans *et al.,* (2010). This was achieved through the comparability of diagentically altered bone and dentine values (which should reflect the $^{87}Sr/^{86}Sr$ of the ancient pore fluid at, or shortly after, burial) with modern proxy values, including significantly the mineral water samples from Montgomery *et al.*(2006), which by definition must be free of modern pollutants. Whether modern pollutants and fertilisers are changing this validation in certain locations is still debatable (considering Crowley *et al.,* 2015). Careful sampling can avoid most modern day bias in the biosphere, but sometimes this is not possible and so it is better to acknowledge their presence and possible contribution during interpretations of modern biosphere $^{87}Sr/^{86}Sr$ data.

2.3. The Sr-isotopes of Britain

2.3.1. The Sr-isotope biosphere map of Britain

A preliminary Sr-isotope biosphere map of Britain has been produced by Evans *et al.* (2010) and can be seen in Figure 1.1 in chapter 1. This map of Britain displays a range of $^{87}Sr/^{86}Sr$ between 0.707 and 0.720, although the highest value is only found in a few isolated localities. Table 1 in Evans *et al.* (2010, p.3) displays the average biosphere $^{87}Sr/^{86}Sr$ values used to construct the Sr-isotope biosphere packages, which have been categorised by the age of bedrock geology. The method of using package domains over a contoured map was preferred as the biosphere $^{87}Sr/^{86}Sr$ data displayed no systematic gradational change and could show a lot of overlap in heterogeneous areas (determined in and discussed by Evans *et al.,* 2009, p.627-628). The BGS 1:625000 Bedrock Geology map of Britain (2007) was also used to extrapolate $^{87}Sr/^{86}Sr$ packages across large areas of the country, under the assumption that bedrock geology drives the variation of biosphere $^{87}Sr/^{86}Sr$. The limitations of this map are stated clearly by Evans *et al.* (2010), in that the Sr-isotope data available was limited at time of creation and also resulted in non-systematic coverage of Britain (hence the extrapolations). As more Sr-isotope biosphere data becomes available the Sr-isotope biosphere map of Britain will be refined, with further preparations being taken to produce an interactive multi-isotope map of Britain by Evans *et al.* (in prep; Evans, *pers.com.*).

There is an approximate south-east to north-west trend towards higher $^{87}Sr/^{86}Sr$ values across the Sr-isotope packages in Britain (Figure 1.1 in chapter 1). The lower values of around 0.708-0.710 occur along the east coast and south-east of England, followed by the 0.710-0.713 values of south-west England and Wales, to the high and heterogeneous values >0.713 in northern Scotland, with the exception of the values <0.708 found on the Isle of Skye and Isle of Mull, Scotland.

Since Evans *et al.* (2010) further extensive studies have produced biosphere $^{87}Sr/^{86}Sr$ data, either to aid in their own migration or mobility study or to supplement the biosphere Sr-isotope map of Britain. Chenery *et al.* (2010), based on Roman Gloucester, were published in the same year as Evans *et al.,* (2010). Plant samples were collected within a 30km radius of the city of Gloucester, with $^{87}Sr/^{86}Sr$ values ranging from 0.70767 to 0.71622 and a mean of 0.7109± 0.0045 (n=34, 2SD). The wide range in plant $^{87}Sr/^{86}Sr$ reflects the complex bedrock geology in the area. The higher values >0.714 are on Precambrian plutonic igneous and metamorphic rocks of the Malvern Hills. Overall though, the Malvern Hills have a mean plant $^{87}Sr/^{86}Sr$ = 0.7128 ±0.0040 (n=13, 2SD). To the west of Gloucester, on Jurassic sedimentary rocks (with tidal flood deposits of the river Severn) the mean plant $^{87}Sr/^{86}Sr$ = 0.7095 ±0.0012 (n=8, 2SD), while to the east the Jurassic Limestone bedrock of the Cotswolds have plant $^{87}Sr/^{86}Sr$ = 0.7088 ±0.0025 (n=8, 2SD).

A doctoral thesis by Warham (2011) focused on eastern England where little biosphere $^{87}S/^{86}Sr$ data had previously been collected. The bedrock geology of eastern England mainly consists of Jurassic mud-, silt-, sandstones, Cretaceous Chalk and Cretaceous mud-, sand- and limestones. The $^{87}Sr/^{86}Sr$ values range from 0.707 to 0.711, although a value at 0.711394 is a singular occurrence. The biosphere $^{87}S/^{86}Sr$ above the Jurassic sedimentary lithologies display a larger range of values, from 0.708-0.711, compared to the Cretaceous carbonate lithologies (e.g. chalk and limestone lithologies), at 0.707-0.709. Just the Cretaceous Chalks have biosphere $^{87}S/^{86}Sr$ = 0.708 ±0.0008 (n=14, 2SD) (Warham, 2011, p.125).

Boulton (2011: and one of the authors in Evans *et al.,* 2010) collected further plant samples to supplement and refine the biosphere Sr-isotopes of the UK. These were collected from across the Midland Valley and Southern Uplands terranes of Scotland, which approximately covers the counties of West Dunbartonshire, in and around the city of Glasgow, Renfrewshire and Lanarkshire. The plant $^{87}Sr/^{86}Sr$ values range from 0.7061 -

0.7148 (n=51), with the lowest values, at 0.706 -0.708 (n=8), concentrating in the county of Renfrewshire and the highest values, at 0.713-0.714 (n=4) occurring in south Lanarkshire. In Montgomery *et al*. (2014) further plant samples were collected from Westness, Orkney, Scotland, with plant $^{87}Sr/^{86}Sr$ = 0.70996 ±0.00079 (n=7, 2SD), which compare with the values already from Orkney in Evans *et al.* (2010). The Isle of Man has also had its first published Sr-isotope biosphere data in Hemer *et al.* (2014), which includes three plant samples across the island with $^{87}Sr/^{86}Sr$ = 0.7091, 0.7104 and 0.7113 and one dentine sample from a skeleton (BD 24) buried in Balladoole cemetery with $^{87}Sr/^{86}Sr$ at 0.7092. The lower $^{87}Sr/^{86}Sr$ values are similar to the marine value (~0.7092: Veizer, 1989, p.142) and are situated on the west to south-west side of the island, while the higher values >0.710 are on the east to north-east side and probably reflect a combination of the geologically derived and marine derived Sr.

A transect through southern Wales, from the Malvern Hills in England, through the Welsh border and on to the south-west of Wales towards Newport has also produced plant $^{87}Sr/^{86}Sr$ data (Neil *et al.,*2017: Evans, unpublished results; pers.com.). The bedrock geology dates from the Precambrian to the Triassic, mainly covering the Siluro-Devonian Old Red Sandstones (ORS) and the Silurian sedimentary rock. A few igneous lithologies were also sampled from, such as Ordovician Igneous tuffs near Newport, Wales, and the Precambrian Igneous rocks of the Malvern Hills, England. The plant $^{87}Sr/^{86}Sr$ values range from 0.708 to 0.715. The highest value comes from the Precambrian Igneous rocks from the Malvern Hills and lowest value from the Silurian sedimentary rocks in Wales; both are found as single occurrences and so a range of 0.709 to 0.713 is a better reflection of the biosphere $^{87}Sr/^{86}Sr$ across this transect. There are also four plant samples (USK-01 to 04) collected in the county of Powys, Wales, on the Silurian Ludlow bedrock, which mainly consist of mudstones. The plant $^{87}Sr/^{86}Sr$ = 0.71012, 0.71230, 0.71334 and 0.71550 on this Silurian bedrock and the highest value was taken at Hell's Mouth, Powys, Wales, in a woodland setting (Evans, *pers.com*.).

There are also 20 plant samples collected to the north of Derby on the Carboniferous sedimentary bedrock (which includes the Millstone Grit Group and Pennine Coal Measures). The plant $^{87}Sr/^{86}Sr$ ranges from 0.7091 - 0.7154, although the highest value is a single occurrence and so 0.7091 - 0.7128 is a better representation of the values over this area (NIGL, unpublished results). Overall none of these more recent studies have produced biosphere $^{87}Sr/^{86}Sr$ values >0.716.

A doctoral thesis by Snoeck C. (not yet available) and a published study by Snoeck *et al.* (2016) provide biosphere data for Northern Ireland. In their study, Figure 4 (p. 402) displays the biosphere $^{87}Sr/^{86}Sr$ in packages similar to Evans *et al.* (2010) and is based on 88 plant samples taken from 40 locations across Northern Ireland. The lowest values of 0.7052-0.7068 are found in the north-east to east, mainly over the Palaeocene basalts, while the highest values >0.7115 are found to the south/south-east, on the Silurian to Devonian and Tertiary granite intrusions, and to the north on the Precambrian Dalradian metasedimentary rocks. There are currently four plant samples in Northern Ireland with $^{87}Sr/^{86}Sr$ >0.714.

When describing $^{87}Sr/^{86}Sr$ values, higher ratios are often referred to as more radiogenic retrospective to lower ratios, regardless of whether the value is from a biosphere proxy or an animal or a human skeletal sample. In Britain, any values >0.714 are often described as radiogenic in comparison to the majority of known British $^{87}Sr/^{86}Sr$ values which are <0.713 (Evans *et al.,* 2010; Evans *et al.,* 2012). Table 2.1 contains all the biosphere $^{87}Sr/^{86}Sr$ values >0.714 currently available in Britain (Evans *et al.,* 2009; 2010; Chenery *et al.,* 2010; Boulton, 2011; Snoeck *et al.,* 2016; Evans, *pers.com.*). This table does not include the ground water and stream water $^{87}Sr/^{86}Sr$ values >0.714 in Shand *et al.* (2007), as no coordinate data was available for them. In Shand *et al.* (2007), three stream water and 18 ground water samples record values between 0.71402 -0.71521 and all are on the Lower Palaeozoic (Ordovician to Silurian) mudstone and shales of the Plynlimon catchment in the Cambrian mountains, central Wales. Just the ground-waters on the Ordovician bedrock are reported in Evans *et al.* (2010) as having $^{87}Sr/^{86}Sr$ = 0.7130 ±0.0008 (n=11, 1SD).

From Table 2.1, Shand *et al.* (2007) and the preliminary Sr-isotope biosphere map of Britain, Scotland is where the majority of biosphere $^{87}Sr/^{86}Sr$ >0.714 are found, specifically the Cairngorm mountain range in the Cairngorms National Park (central Scotland) and in the Northern Highlands. The bedrock geology of the Cairngorms National Park mainly consists of the Siluro-Devonian granites and the Precambrian Dalradian metasediments, while in the Northern Highlands Precambrian Lewisian gneisses and Precambrian Dalradian metasediments dominate.

There are only five samples (three plant and two water) with $^{87}Sr/^{86}Sr$ values >0.720 in Britain, making them a rare find, and they are all in Scotland. The first plant sample (0.72660) was collected just north of the Cairngorm mountain range, and could potential be explained by the erosion of the extensive granitic rocks that form these mountains. The other two plant samples (0.72093 and 0.72513) and one water sample (0.72065) are situated on the Precambrian Dalradian metasediments of the central Scotland. These were plotted as hotspots in Evans *et al.* (2010) because there is no obvious lithological reason for their high values. The last water sample (0.72335) is on the Precambrian (Archean) granites and gneisses from the Outer Hebrides, Scotland. This high water $^{87}Sr/^{86}Sr$ value has not been repeated in the overall biosphere $^{87}Sr/^{86}Sr$ on the Outer Hebrides, which instead reflects the sea-spray and Quaternary machair deposits (~0.70925 - 0.71025: Montgomery *et al.,* 2003; Evans *et al*., 2010).

In England and Wales a few plant samples have produced $^{87}Sr/^{86}Sr$ between 0.714 -0.716 (Table 2.1). Five of these plants are located at the Malvern Hills, England, on the Precambrian Malvern Complex (Chenery *et al.,* 2010; Evans*,* unpublished results; *pers.com*.), and one plant sample is rooted into the Millstone Grit, just south of Matlock in Derbyshire, England (NIGL, unpublished results). In Wales, two plant samples have $^{87}Sr/^{86}Sr$ >0.714, one from the Cambrian mountains, just south-west of the town of Llanidloes (Evans *et al.,* 2010) and one from Hell's Mouth, north-west of Boughrood, Powys (Evans, *pers.com.*) and both are situated on Silurian sedimentary bedrock. Then there are also the 18 ground and three stream water samples on the Lower Palaeozoic mudstone and shales in central Wales with values >0.714 (Shand *et al.,* 2007). Whether plant $^{87}Sr/^{86}Sr$ can produce similar values >0.714 on the same bedrock geology in central Wales is unknown at present.

Overall, there are areas in Scotland and a few potential locations within England and Wales that can produce high biosphere $^{87}Sr/^{86}Sr$ >0.714. However, what $^{87}Sr/^{86}Sr$ values can be achieved consistently in the biosphere still needs further study, as at present the most radiogenic packages created for the Sr-isotope biosphere map of Britain have the values of 0.713 - 0.720 (pink) or >0.720 (red) (Evans *et al.,* 2010). One aim of this current study is to see whether the pink package, at 0.713 -0.720, could be split into smaller magnitudes, although it is understood that the heterogeneous nature of the bedrock lithologies that produce such values could make this problematic. It is probably that the Sr-isotope packages already defined in Evans *et al.* (2010) are the best way to display biosphere $^{87}Sr/^{86}Sr$ >0.714.

2.3.2. Human $^{87}Sr/^{86}Sr$ values in Britain

A review of the published data for archaeological humans excavated in Britain was produced by Evans *et al.,* (2012) and is shown in Figure 2.3. Their study included 614 archaeological humans, with a mean $^{87}Sr/^{86}Sr$ = 0.7099 ±0.0026 (2SD) and a range from 0.7064 to 0.7205. However, excluding the humans deemed to be of non-British origin, the human $^{87}Sr/^{86}Sr$ range reduces to 0.7078 - 0.7165 with a median value of 0.7096 and an interquartile range of ±0.0014 (Figure 2.4). Overall, their study highlighted that humans with $^{87}Sr/^{86}Sr$ values >0.714 are rare in Britain. In Scotland the local maximum for human $^{87}Sr/^{86}Sr$ was c.0.7165, based on a Medieval individual PH SK 71 from Parliament House site, Edinburgh, while in England and Wales the maximum was c.0.7140, based on the Medieval humans buried at Hereford Cathedral and a single individual buried at Blackfriars cemetery, Gloucester. Since Evans *et al.* published their review in 2012, more archaeological humans with higher values >0.714 have been excavated in Britain (Parker Pearson *et al.,* 2016; Neil *et al.,* 2017), but there are still no populations with values over 0.7165 in Britain that are deemed to be of local origin and can be explained by the local geology or any other peculiarities in the biosphere.

There are many reason why there is bias in Britain towards finding people with low $^{87}Sr/^{86}Sr$ <0.710 and it is mainly due to carbonates. Carbonate rocks (like limestone, dolomite, etc.) with their low whole-rock $^{87}Sr/^{86}Sr$ and high Sr concentrations tend to be easily weathered and dominate the Sr-isotope biosphere. In addition, these carbonates tend to preserve archaeological bone well, provide the best agricultural land and are often found at lower elevations, so are favourable places for people to live and thrive. A further bias towards low $^{87}Sr/^{86}Sr$ in humans, comes from the contribution of heavy rainfall that affects much of western Britain and results in soils dominated by rainwater Sr (c. 0.7092) rather than geological Sr from the bedrock (Montgomery *et al*., 2014). Any plants grown in such soils will also obtain $^{87}Sr/^{86}Sr$ values similar to rainwater and as plants are the dominant dietary Sr in animals and humans (Burton & Wright, 1995; Montgomery, 2010), such values are passed on to them.

The older silicate lithologies that crop out extensively in western and northern Britain, such as Precambrian Dalradian metasediments and Silurian granite intrusions in Scotland, have a much wider, and usually higher, range of whole-rock $^{87}Sr/^{86}Sr$ and Sr concentrations compared to the carbonate lithologies. However, these whole-rock values are often not reflected in the biosphere $^{87}Sr/^{86}Sr$ on silicate lithologies. Furthermore, soils on silicate lithologies tend to be acidic so bone preservation is poor and so there are no *in situ* representations of archaeological human $^{87}Sr/^{86}Sr$ from such areas. In addition acidic land is often not suitable for agriculture and found at higher elevations, which are not desirable places for humans to live.

Whether any further biosphere $^{87}Sr/^{86}Sr$ >0.714 can be found within Britain could change interpretations of human $^{87}Sr/^{86}Sr$ and the potential maximum biosphere value to be considered British. This will not replace the need for more *in situ* human $^{87}Sr/^{86}Sr$ on granitic terrains, but as none currently exist, the maximum $^{87}Sr/^{86}Sr$ available in the biosphere is the best solution.

2.4. Understanding high $^{87}Sr/^{86}Sr$ biospheres

2.4.1. Producing high $^{87}Sr/^{86}Sr$ >0.714 in the biosphere

All the ^{87}Sr and ^{86}Sr in the biosphere currently originated from bedrock, or specifically certain minerals within the bedrock. ^{86}Sr has remained constant through Earth history, but ^{87}Sr, being radiogenic, has not, which has lead to different $^{87}Sr/^{86}Sr$ originating in different rocks. These differences are characterised by the initial Rb/Sr ratio of the rock when it first crystallised from the mantle, the age of the rock, and hence how much ^{87}Sr has accumulated from the β-decay of ^{87}Rb, and the rocks geological history. Rb and Sr are relatively mobile elements, so any tectonic, metamorphic, magmatic or sedimentary processes, particularly if hydrothermal fluids are involved, can alter the initial Rb/Sr ratio of a rock by taking away old or introducing new ^{87}Rb or ^{87}Sr (Faure,1986, p.118-121; Dickin, 1995; Faure & Mensing, 2005, p.76-80). Depending on what minerals are present within a rock will also affect its Sr concentration (ppm/mgkg^{-1}). Rubidium (Rb^{+1}) can substitute for potassium (K^{+1}) in K-bearing minerals, such as silicate mica minerals (muscovite, biotite, etc.) and K-feldspar, due to similar ionic radii (152pm vs. 138pm respectively: Greenwood & Earnshaw, 2005, p.75ff). As ^{87}Rb β-decays to ^{87}Sr, Rb- or K-bearing minerals that are common in felsic rocks tend to have higher whole-rock $^{87}Sr/^{86}Sr$ values (>1.0). However, it is these K-bearing minerals that often have lower Sr concentrations compared to Sr- or Ca-bearing minerals found commonly in mafic and carbonate rocks (Faure, 1986, p.118; Bentley, 2006, p.139-141).

Age is another dependant factor to consider. Typically, older rocks have higher whole rock $^{87}Sr/^{86}Sr$ values than younger rocks, if they contain higher concentrations of Rb-bearing minerals. If no ^{87}Rb was incorporated into the rock at formation then it will show the original $^{87}Sr/^{86}Sr$ value of the mantle at its time of formation. The $^{87}Sr/^{86}Sr$ value for "primordial" Earth, when it could be considered homogenous, was 0.699 (Wasserburg *et al*.,1969; Faure, 1986, p.161). Slowly ^{87}Sr has been continually increasing through time and so the present day mantle is considered to have $^{87}Sr/^{86}Sr$ at 0.704 ± 0.002. The whole-rock $^{87}Sr/^{86}Sr$ from terrestrial bedrocks can vary from ~ 0.703 for young, volcanic island rocks, mainly mafic in composition, to >0.750, or even >1.0, for K-rich (and hence Rb-rich), igneous granites formed from older, crustal rocks, which are felsic in composition. Oceanic marine carbonates, such as limestones and dolomites, have whole-rock $^{87}Sr/^{86}Sr$ values that reflect the composition of the ocean during their deposition (Faure, 1986, p.161-164; Graustein, 1989, p.495; Bentley, 2006, p.139-141). The $^{87}Sr/^{86}Sr$ released from the bedrock will be dependent on what minerals within the rock are weathered. This can lead to a striking difference between the whole-rock value and the biosphere $^{87}Sr/^{86}Sr$ overlying the same bedrock lithology. Homogenous rocks, which are mainly composed of one or very few minerals, such as limestone and dolomite, are often an exception as they can release $^{87}Sr/^{86}Sr$ that is reflective of their whole rock value due to their simple chemical composition. Many rocks are heterogeneous and polymineralic, resulting in their whole-rock $^{87}Sr/^{86}Sr$ varying across the entirety of the strata or intrusion. The $^{87}Sr/^{86}Sr$ released into the biosphere tends to be lower in value compared to the whole rock value, because the minerals with low $^{87}Sr/^{86}Sr$ values <0.714, e.g. the Sr- and Ca-bearing minerals such as calcite, plagioclase, etc., are more readily weathered out and made bioavailable in the biosphere. Over long time-scales the bedrock can become more enriched in radiogenic ^{87}Sr, simply due to the decay of ^{87}Rb and because minerals enriched with ^{87}Sr, e.g. Rb- and K-bearing minerals, are more resistant to weathering processes and remain within the rock (Faure, 1986, p.183-184). However, this also means that high $^{87}Sr/^{86}Sr$ values are not as bioavailable in the biosphere. There is an exception with the mica minerals, biotite and muscovite. They are generally more susceptible to weathering, compared to the feldspars and quartz for example, and tend to have very high $^{87}Sr/^{86}Sr$ (often >1.0, examples in Clauer, 1981; Hampton & Taylor, 1983; Blum &

Erel, 1997; Dijkstra *et al*., 2003; Sjögren *et al.,* 2009, p.90), as well as high Sr concentrations. Soils (or superficial deposits) that are derived from bedrock with high portions of the mineral biotite and are less than ~20,000 years old, tend to have dramatically elevated $^{87}Sr/^{86}Sr$ because of the preferential weathering of the mica mineral. This means that high $^{87}Sr/^{86}Sr$ values become more bioavailable in the biosphere, until they are leached away with time (Blum *et al.* 1994; Blum & Erel, 1997).

So herein lies the first main obstacle when trying to find and define high Sr-isotope biospheres: the bedrock needs to contain and release $^{87}Sr/^{86}Sr$ >0.714 that is bioavailable in the biosphere. The best lithologies, in terms of mineral composition, are felsic igneous rocks, such as granites (or their smaller crystal or metamorphic equivalents) that contain high portions of Rb- and K-bearing minerals, and the older the rock the better, to allow for more decay of ^{87}Rb, meaning Precambrian rocks are often best in terms of age. Age is not always a strict requirement, but the composition of the lithology is, as the rock needs to have high initial proportions of ^{87}Rb, to produce high $^{87}Sr/^{86}Sr$ >0.714. Once released and made bioavailable, such high $^{87}Sr/^{86}Sr$ then needs to compete with all the other Sr inputs in the biosphere. It has been calculated that only 0.2 to 20ppm of the bioavailable Sr-isotopes in soils are accessible to plants (Åberg *et al.*, 1990; Capo *et al.,* 1998; Bentley, 2006, p.140; Frei, 2012, p.114) and plants are the dominant dietary Sr in animals and humans (Burton & Wright, 1995; Montgomery, 2010). Often, high $^{87}Sr/^{86}Sr$ >1.0 from granitic lithologies have low Sr concentrations and so are susceptible to being masked by a variety of different Sr-isotope inputs within the biosphere with higher Sr-isotope concentrations. Therefore, any high $^{87}Sr/^{86}Sr$ released from the bedrock needs to dominant the biosphere completely if animals or humans are to acquire such high $^{87}Sr/^{86}Sr$ values themselves.

Animals and humans are not passive receptors of environmental Sr-isotopes either, making choices on where and when they source components of their diet. They effectively average the $^{87}Sr/^{86}Sr$ accessible to them through their diet (which is dominantly through plants: Burton & Wright, 1995; Montgomery, 2010). This effect increases further up the food chain, which means herbivores can show a larger range of $^{87}Sr/^{86}Sr$ compared to carnivores (Burton *et al.,* 1999; Blum *et al.* 2000; Bentley, 2006, p.148-150, 154-155). Overall though, to achieved values >0.714 animals and humans need to be consistently consuming from biospheres equal to or ideally greater than their $^{87}Sr/^{86}Sr$ to combat this averaging effect.

2.4.2. Case studies of high Sr-isotope biospheres in Europe

In Europe high Sr-isotopes biospheres with values >0.714 have been found overlying the bedrock geology of the Baltic Shield, which in its entirety covers Sweden, southern Norway, Finland, into Northern Denmark, onwards into northwest Russia and under the Baltic sea and is shown in Figure 2.5. The Baltic Shield contains some of the oldest rocks in Europe, with some dating to the Archean of the Precambrian (>2.5 billion years old), but the majority date within the Proterozoic of the Precambrian (~0.5-2.5 billion years old). The main lithologies include granites and strongly metamorphic gneisses.

The bedrock geology of Sweden is dominated by Precambrian granite and gneiss lithologies, which have whole rock $^{87}Sr/^{86}Sr$ = 0.709 - 0.94 and 0.711 - 1.206 respectively (Sjögren *et al.,* 2009). Biosphere $^{87}Sr/^{86}Sr$ data in Sweden regularly records values ranging from 0.714 to >0.720 (Åberg & Wickman, 1987; Åberg *et al*., 1989; Poszwa *et al.,* 2004; Sjögren *et al.,* 2009*;* Price *et al.,* 2012a ; Sjögren & Price, 2013; Frei *et al.* 2009; Price *et al.,* 2017). Such high values have also been recorded from archaeological animals and humans (Sjögren *et al.,* 2009*;* Sjögren & Price, 2013; Price *et al.,* 2017). Similar to Britain, finding well preserved human skeletal remains in the soils overlying the acidic rocks of the Precambrian has been noted as challenging, but where Britain has not excavated any humans with $^{87}Sr/^{86}Sr$ >0.720 *in situ* to such environments, several humans have been excavated and analysed *in situ* recording $^{87}Sr/^{86}Sr$ >0.720 (Sjögren *et al.,* 2009*;* Price *et al.,* 2017). Even inland in the limestone region of Falbygden archaeological non-domesticated fauna and modern snail shell biosphere have recorded $^{87}Sr/^{86}Sr$ values between 0.7120 - 0.7159 (Sjögren *et al.,* 2009; Sjögren & Price, 2013). These values were considered somewhat higher and more variable than usually produced from this lithology, but Sjögren *et al*.(2009) and Sjögren & Price (2013) suggest that the large glacial deposits that cover Falbygden contain crystalline material from the Precambrian granites and gneisses from the north and make a more radiogenic contribution. The weathering of the Precambrian bedrock in Sweden has also influenced the $^{87}Sr/^{86}Sr$ of precipitation, with Åberg *et al*. (1989) reporting inland values between 0.710 - 0.719 from rain and snow from Hagfors (n=6). Another study by Andersson *et al.* (1990) analysed snow across the Scandinavian Peninsula covering a 450km transect from the Atlantic Ocean to the Gulf of Bothnia. The $^{87}Sr/^{86}Sr$ of the snow varied across the sampling stations, from 0.7098 near the Atlantic to 0.7194 at the most eastern station. These have substantially deviated from the marine value (c.0.7092: Veizer, 1989, p.142).

The island of Bornholm, Denmark, has also produced high biosphere $^{87}Sr/^{86}Sr$ >0.72 (Frei & Frei, 2011; 2013; Price *et al.,* 2011; Price *et al.,* 2012a). Although Frei & Frei (2013) state there were some exceptions, generally the biosphere overlying the Precambrian bedrock of the Baltic Shield (granites and gneisses) provided the highest $^{87}Sr/^{86}Sr$ values, which are located on the north side of the island. A discussion into the potential effects of sea spray on the island by the authors has them questioning if the biosphere $^{87}Sr/^{86}Sr$ values recorded were lower than expected, as whole rock $^{87}Sr/^{86}Sr$ = 0.757 - 0.945 for the Precambrian granites and gneisses on the island. The bedrock geology to the south of the island consists of Cambro-Silurian and Triassic to Cretaceous sedimentary rocks and a lot of the island is also covered with Quaternary glacial deposits. The Precambrian rocks are exposed to the north of the island and only have a thin Quaternary sediment cover, while in the south the Phanerozoic sedimentary rocks are covered with glacial till which contains eroded material from the Precambrian rocks further north (Frei & Frei, 2013, p.148-150). The analysis of surface waters from across the island have $^{87}Sr/^{86}Sr$ values ranging from 0.7097 - 0.7281, with a mean of 0.7175 ±0.005 (1SD), while soil extracts ranged from 0.7095 - 0.7197, with a lower mean of 0.7125 ±0.003 (1SD). Altogether samples collected from the northern part of Bornholm only, and so dominated by Precambrian granites and gneisses have a mean of 0.7161 ±0.0049 (n=37, 1SD), while those to the south on the Phanerozoic sedimentary rocks have a mean of 0.71101 ±0.0013 (n=10, 1SD) (Frei & Frei, 2013).

Mainland Denmark Sr-isotope biospheres record much lower $^{87}Sr/^{86}Sr$ values ranging from 0.707 - 0.7128 (Frei *et al.*, 2009; Frei & Frei, 2011; Price *et al*., 2011; Frei, 2012; Frei & Price, 2012). These values are also recorded in archaeological humans considered to local to Denmark too (Price *et al*., 2012b; Frei & Price, 2012). Despite the immense Quaternary glacial deposits across Denmark, often containing material from the Precambrian Baltic Shield, high values from mainland Denmark have not been reported. Any archaeological humans in Denmark reported with values >0.714 are described as being local to older geological terrains, often noting those from Sweden, Norway or the outcrops present of the island of Bornholm, Denmark (Price *et al.,* 2011; Price *et al.,* 2012a; 2012b).Norway has sparse biosphere $^{87}Sr/^{86}Sr$ data currently. A single modern sheep wool sample and a single soil sample were reported from Hemsedal, Norway, and have values at 0.7051 and 0.7045 respectively (Frei *et al.*, 2009). Mineral waters from Norway have $^{87}Sr/^{86}Sr$ between 0.707-0.709 (n=2) and >0.72 (n=2) (Voerkelius *et al.*, 2010). Four medieval humans in Åberg *et al.,* (1998) have enamel $^{87}Sr/^{86}Sr$ = 0.71976, 0.71985, 0.72359 and 0.73232. These four medieval humans are from inland sites within Norway and have higher $^{87}Sr/^{86}Sr$ than the medieval human situated at a coast site, with enamel $^{87}Sr/^{86}Sr$ = 0.71087. Åberg *et al.* (1998) state that the medieval humans that lived inland, most likely from farming communities, have $^{87}Sr/^{86}Sr$ reflective of the bedrock geology, e.g. the Precambrian Baltic Shield (so granites and gneisses). A modern human tooth sample dating to the 1970s from Ringebu, a small farming village in the valley of Gudbrandsdalen in north Norway, also had high value of 0.71769: the medieval counterparts from this village recorded the value of 0.71976 and 0.72359 above. Similar to Sweden, Norway seems to produce higher $^{87}Sr/^{86}Sr$ values inland compared to the coast, where, regardless of the bedrock geology, marine $^{87}Sr/^{86}Sr$ value can dominant. This is not a consistent trend in either country, for example Norway has recorded values of 0.7045 and 0.7051 inland at Hemsedal by Frei *et al.* (2009).

The whole rock $^{87}Sr/^{86}Sr$ from Precambrian bedrock in Finland regularly records values greater than 0.720, with a median values range from 0.7135 - 0.7637 (Kaislaniemi, 2011), so far though Finland has a limited amount of biosphere $^{87}Sr/^{86}Sr$ data . Åberg and Wickman (1987) analysed 45 rivers draining Northern Sweden and Finland with $^{87}Sr/^{86}Sr$ values varying from 0.7177-0.7366, while natural mineral waters from Finland have recorded $^{87}Sr/^{86}Sr$ >0.720 (n=4) (Voerkelius *et al*., 2010).

The occurrences of high biosphere $^{87}Sr/^{86}Sr$ >0.714 lessens and values >0.720 are rare, outside of the bedrock geology of the Baltic Shield in Europe. However, not many extensive Sr-isotope biosphere maps have been produced across Europe and some countries have more biosphere data published than others. To date, high biosphere $^{87}Sr/^{86}Sr$ have mainly been recorded around the Bohemian Massif and around igneous and metamorphic intrusions of the Black Forest in Germany, the Central Massif in France, and the Iberian Massif of Portugal and Spain, which all formed during the Variscan Orogeny in the Carboniferous (Neubauer, 2009, p.199-201), as well as the Central Alps (Figure 2.5).

In Germany $^{87}Sr/^{86}Sr$ between 0.71168 to 0.71866 have been reported from ground, river and mine water from Freiberg, in Saxony (Tichomirowa *et al.,* 2010), which is based on the granitic and metamorphic lithologies of the Bohemian Massif to the east.

Mineral water samples from a similar area have $^{87}Sr/^{86}Sr$ ranging from 0.711 to >0.720 (Voerkelius *et al.,* 2010). Archaeological pig enamel from the Bavarian Forest, further to the south and still on the granitic and metamorphic lithologies of the Bohemian Massif, have a mean $^{87}Sr/^{86}Sr$ = 0.7202 ±0.0035 (n=6: Bentley & Knipper, 2005). In southern Germany to the west where the Black Forest and River Rhine are situated, along with the Vosges Mountains of France, mineral and stream water and soil solutions have $^{87}Sr/^{86}Sr$ = 0.717 - 0.725 and are on the igneous intrusions that were part of the Variscan Orogeny, mainly granite, granodiorite and their metamorphic equivalents (Bentley *et al.,* 2003; Voerkelius *et al.*, 2010). Archaeological pig enamel from medieval sites in the Black Forest have mean $^{87}Sr/^{86}Sr$ = 0.7163 ±0.0021 (n=7: Bentley & Knipper, 2005), while modern snail and plant samples across the granites and gneisses have mean $^{87}Sr/^{86}Sr$ = 0.71453 ±0.00313 (n=8, 1SD) and 0.71525 ±0.00293 (n=9, 1SD) respectively (Oelze *et al.,* 2012). Further south, the Alps mountain range, have stream water $^{87}Sr/^{86}Sr$ = 0.720 - 0.724, on the gneiss bedrock of Central Alps around Längefeld, Naturns and Tschars, while human skull samples from the same area, which have probably been diagenetical altered, have $^{87}Sr/^{86}Sr$ = 0.712 - 0.732 (Hoggewerff *et al.,* 2001).

Willmes *et al.* (2014) have recently produced an extensive Sr-isotope biosphere map for France, which can be seen in Figure 2.6. Their Isotopic Reconstruction of Human Migration (IRHUM) database allows access and ability to explore and map the plant and soil samples used to characterise the biosphere across France. High $^{87}Sr/^{86}Sr$ >0.714, with a maximum value of approximately 0.744, are recorded by plant samples (mainly grass, moss and other low-lying plants) on and around Central Massif, where granites and gneisses dominate the bedrock geology. The higher plant values >0.72 are found in the uplands of the Central Massif with only a few rare occurrences in the lowlands. Plant $^{87}Sr/^{86}Sr$ >0.714 are found on the Armorican Massif of western France, south of Brittany and to the south along the Pyrenees that separate France from Spain. However, these values are sporadic, occurring alongside lower plant $^{87}Sr/^{86}Sr$ <0.713, with many values being very similar to the marine value (c.0.7092: Veizer, 1989, p.142) as a result of being so near to the coast.

Each plant sample had a accompanying soil sample analysed, in which the $^{87}Sr/^{86}Sr$ values were mostly similar to the plants (Willmes *et al,* 2014). However, a trend of the soils having lower $^{87}Sr/^{86}Sr$ values has been observed, with a difference -0.02 in extreme cases between plant and soil samples taken at the same location. Difference of -0.002-

0.005 are more common. It is probably that the plant samples are a better reflection the $^{87}Sr/^{86}Sr$ available in the biosphere and to humans and animals, than the soil samples. Another trend seen in the high biosphere $^{87}Sr/^{86}Sr$ of France, is that values can range largely over relatively short distances. For example, an approximate 30km transect from Lempdes-sur-Allagnon to Arlanc have plant $^{87}Sr/^{86}Sr$ that varies from 0.7146 to 0.7259, which reflects the different bedrock lithologies and their heterogeneous nature.

The isotope package assigned to the upland areas of the Central Massif have biosphere $^{87}Sr/^{86}Sr$ = 0.7141 - 0.7200 (red package) (Figure 2.6). This indicates that Willmes *et al.* (2014) are not confident to assign any areas in France as having biosphere $^{87}Sr/^{86}Sr$ >0.72. This is understandable as such values are sporadic across France. Rainwater collected from the Central Massif over a one year period have $^{87}Sr/^{86}Sr$ = 0.7092 - 0.7131 (n=13) (Négrel & Roy, 1998). The change in rainwater $^{87}Sr/^{86}Sr$ values have been interpreted as the changing influence of terrestrial dust from different bedrock sources (Négrel and Roy, 1998). The mean $^{87}Sr/^{86}Sr$ of these rainwater samples is 0.7104, which still shows that the terrestrial dust has significantly shifted the mean annual rainwater value from the marine value (c.0.7092: Veizer, 1989, p142) by +0.0012. Rainwater from the Vosges mountain range have $^{87}Sr/^{86}Sr$ = 0.7096 - 0.7114 across several years (Probst *et al.*, 2000) again deviating from the marine value by approximately +0.0004 to +0.0022.

The Iberian Massif of Portugal and western Spain have mineral water $^{87}Sr/^{86}Sr$ = 0.713 - >0.720 (Voerkelius *et al.,* 2010). Archaeological fauna from La Pijotilla, a Copper Age site (c. 3300-2100 cal BC) in the province of Badajoz in south-west Spain, record enamel $^{87}Sr/^{86}Sr$ = 0.71477 ±0.00030 (n=4, 1SD), while human enamel $^{87}Sr/^{86}Sr$ ranged from 0.70972 - 0.71612 (n=17). However, only the humans with values between 0.712-0.715 were considered local to the site (n=12), which is on Tertiary conglomerates and sandstones, but with a variety of gneisses found just south of the site. Non-locals consisted of one individual >0.715, at 0.71612 and four <0.712, at 0.70972, 0.71059, 0.71136 and 0.71168 (Díaz-Zorita Bonilla, 2013, p.186-201). These humans could easily be explained by the complex geology surrounding the site but there is not biosphere $^{87}Sr/^{86}Sr$ data to confirm this though. Another Copper Age site, Valencina-Castilleja, found in the province of Seville south-west Spain on Tertiary conglomerates and the southern tip of the Iberian Massif, has also produced high values >0.714 in human enamel, at 0.71450 and 0.71883, in goat enamel at 0.71611 and from a soil sample at 0.71510; although the author notes to take this value with caution). Local $^{87}Sr/^{86}Sr$ was determined by archaeological fauna, with $^{87}Sr/^{86}Sr$ = 0.708 - 0.710. Potentially these humans and goat dating to the Copper Age originate from the Cambro-Ordovician granitic bedrock found to the north of the Seville province or the metamorphic and plutonic intrusions of the Ossa Morena Zone of the Iberian Massif to the north-west (Díaz-Zorita Bonilla, 2013, p.186-201). Again though there is no biosphere $^{87}Sr/^{86}Sr$ data on these bedrocks to confirm if this observation is correct.

The common trends observed from the case studies of high $^{87}Sr/^{86}Sr$ biospheres from across Europe are as follows: the bedrock geology is dominated by felsic igneous lithologies, such as granites, and their metamorphic equivalents in the form of schists and gneisses; the bedrock geology is geologically old, mainly from the Precambrian to late Palaeozoic (mainly Ordovician to Silurian); the bedrock geology often consists of plutonic intrusions covering several 10s to 100s of kilometres in total.

The granitic lithologies still produce very heterogeneous $^{87}Sr/^{86}Sr$ in the biosphere and can show a lot of overlap with other biosphere $^{87}Sr/^{86}Sr$ from different bedrock geology, sometimes making it difficult to assign a cut off point for local vs. non-local values in humans and animals. Both Sjögren *et al.* (2009) and Sjögren & Price (2013) discuss in depth the implications of drawing a cut-off point for local vs. non-local Sr-isotope values in the limestone region of Falbygden in Sweden, including the feeding and mobility habits of humans, domesticated and non-domesticated animals, and settle on an upper limit of 0.716-0.717 for local individuals to the limestone region. Any values >0.717 are believed to have originated from the surrounding Precambrian gneiss bedrock, based on fauna found along an approximate 100km transect on the same bedrock, which have enamel $^{87}Sr/^{86}Sr$ between 0.71781 - 0.72918. The difference of approximately +0.0114 between the fauna values over the 100km transect displays the heterogeneous nature of the Precambrian gneiss bedrock.

The predominantly granitic lithologies of the bedrock geology can also influence the Quaternary glacial deposits. For example, the limestone region of Falbygden in Sweden is more radiogenic than expected due to the crystalline material in the glacial deposits that extensively cover the region being derived from the Precambrian granites and gneisses in the north (Sjögren *et al.,* 2009). In turn, the glacial deposits erode the Cambro-Silurian sediments of the Falbygden region and deposit them further south on the Precambrian gneisses, producing lower faunal enamel $^{87}Sr/^{86}Sr$ values than expected and become increasingly higher the further away from the Falbygden region they get (Sjögren *et al.,* 2009). However, even if Quaternary glacial deposits are proposed to contain material from the Precambrian Baltic Shield, they do not always influence the biosphere $^{87}Sr/^{86}Sr$: in mainland Denmark no high $^{87}Sr/^{87}Sr$ >0.714 has been recorded despite the extensive covering of glacial deposits (Frei *et al.,* 2009; Frei & Frei, 2011; Price *et al.,* 2011; Frei, 2012; Frei & Price, 2012).

In their investigation of soil profiles in Sweden, Åberg *et al.* (1990) and Åberg (1995) showed that within the first 20cm depth of the soil, the loss of Ca-minerals through weathering, and the enrichment in more resistant K-minerals (rich in radiogenic ^{87}Sr), has resulted in higher $^{87}Sr/^{86}Sr$ values compared to the deeper soil. This seems to be the opposite of the norm, where variability of $^{87}Sr/^{86}Sr$ in the soil profile tends to be caused by increased contributions of atmospheric Sr, with a marine value (c.0.7092: Veizer, 1989, p.142). The first 20cm depth of the soil profile is dominated by the marine value because of the atmospheric input of Sr, but as the soil profile gets deeper the contributions of atmospheric Sr decrease while contributions of bedrock Sr increase (Capo *et al.,* 1998, Vitousek *et al.,* 1999; Probst *et al.,* 2000; Pourcelot *et al.,* 2008; Chadwick *et al.,* 2009). The high $^{87}Sr/^{86}Sr$ >0.714 of precipitation inland in Sweden (Åberg *et al.,* 1989) and inland in Scandinavia in general (Andersson *et al.,* 1990), could also be contributing to the higher $^{87}Sr/^{86}Sr$ seen in the top layer of the soil profiles in Sweden (Åberg *et al.* 1990; Åberg, 1995), as well as aiding in the leaching of Ca-minerals, so this reverse trend in the soil profile is an interesting observation. It could be that a similar 'reverse' trends occurs in the soil profiles of the Central Massif and Vosges mountain range in France, where rainwater has recorded $^{87}Sr/^{86}Sr$ up to 0.713 (Négrel & Roy, 1998; Probst *et al.,* 2000). Overall, the precipitation over these areas of high biosphere $^{87}Sr/^{86}Sr$ seem to be much more radiogenic than the rainwater recorded across Britain, which deviate regionally by ±0.0005 from the marine value of 0.7092 (Warham, 2011, p.150-163).

2.4.3. Other environmental reasons for elevated $^{87}Sr/^{86}Sr$ in the biosphere

Section 2.4 has mainly focused on understanding the bedrock geology needed to release high $^{87}Sr/^{86}Sr$ >0.714 in the biosphere. A few environmental processes have also been observed that have resulted in elevated biosphere $^{87}Sr/^{86}Sr$. For example the leaching Ca-minerals from soils or Quaternary superficial deposits have the potential to increase $^{87}Sr/^{86}Sr$, regardless of the bedrock, with the possible exception of carbonates,, even if it does not necessarily result in values >0.714. The study by Åberg *et al.* (1990) in Sweden described in section 2.4.2, has shown such an increase in $^{87}Sr/^{86}Sr$ within the soil profile because of Ca-weathering, and therefore the loss low $^{87}Sr/^{86}Sr$ values. There are also studies that indicate Ca depletion in soils through the increase of Ca in streams and rivers (Bain & Bacon, 1994; Bailey *et al.,* 1996). Within the doctoral thesis by Warham (2011, p.114-125), superficial deposits labelled Clay-with flints represent an *in situ* weathering product of the Upper Cretaceous Chalk of south-east Britain and are decalcified. These superficial deposits have plant $^{87}Sr/^{86}Sr$ values between 0.7094-0.7098. Warham describes how these values associate more closely with the biosphere data from Jurassic mudstone (0.709-0.711) than the Chalk or other limestone formations (0.707-0.709), overall showing a slight elevation in $^{87}Sr/^{86}Sr$. In heterogeneous biospheres, such as those in Sweden, the increased change in $^{87}Sr/^{86}Sr$ through leaching of Ca-minerals can vary by approximately +0.01-0.03 (Åberg *et al.*, 1990) or in the case of more homogenous biospheres, such as those in south-west Britain documented by Warham (2011, p.120) above, by approximately +0.0002 - 0.0018.

An interesting environmental trend in the studies by Åberg *et al.* (1990) and Warham (2011, p.114-125), is that the biosphere data was collected from a forest or woodland. Organic acid production and increased soil acidity are mechanisms that can influence soil weathering in woodlands (Dijkstra *et al.* 2003; Poszwa *et al.,* 2004). Throughfall, the part of rainfall or other precipitation which falls to the forest floor from the canopy, can have higher $^{87}Sr/^{86}Sr$ and Sr concentrations compared normal precipitation, at 0.7092 (Veizer, 1989, p.142) and <0.4ppm (Figure 2.1: Bentley, 2006, p.140), because it can contain Sr from terrestial dust on the leaves surface (Gosz & Moore, 1989; Poszwa *et al.,* 2000; Probst *et al.,* 2000). Differences between throughfall $^{87}Sr/^{86}Sr$ and normal precipitation $^{87}Sr/^{86}Sr$ range from +0.001 (Gosz & Moore, 1989) to +0.0007-0.0016 (Probst *et al.,* 2000). This may result in the upper part of the soil profile in woodlands being saturated in throughfall $^{87}Sr/^{86}Sr$ values. Overall though, it is expected that the leaf litter produced by a woodland can increase the pH of precipitation, and throughfall, as it percolates through the soil, leading to greater Ca depletion and a mass loss of Ca through time. As most Ca-bearing minerals in the soil have low $^{87}Sr/^{86}Sr$ values, the depletion in Ca can also be seen as a depletion of low $^{87}Sr/^{86}Sr$ values, resulting in the biosphere of the woodlands becoming more radiogenic with time. For easier reference later on in this thesis, this circumstance will be heron in be known as the woodland effect.

2.5. Anthropological reasons for high $^{87}Sr/^{86}Sr$ in humans and animals?

Animals and humans are not passive receptors of environmental Sr, but make choices about when and where they source the components of their diet. Once ingested, different dietary components may contribute more or less to the Sr in the body tissue that is measured. Geological and environmental processes, such as differential weathering, mixing of Sr from different sources and atmospheric deposition (section 2.2 and 2,4), also affect the available Sr. This multiplicity of options and events are distilled into the single measured $^{87}Sr/^{86}Sr$ that is obtained from tissues such as tooth enamel. Attempting to untangle and reconstruct the environmental constraints and culturally-determined actions of people in the past that may lie behind a Sr-isotope ratio is complex, but is the ultimate goal of archaeologists.

When concerning animal and humans in Britain with high $^{87}Sr/^{86}Sr$ >0.714, a lot of focus has been put towards finding geological or environmental explanations for them. However, there are certain aspects of human behaviour not currently taken into account during interpretations of $^{87}Sr/^{86}Sr$. For example, it is widely recognised that tooth wear in archaeological populations was often far greater than today – one of the main reasons for this is believed to be the coarser diet and particularly the presence of soil and rock in their food, included either accidentally via dirt or grit from grinding, or intentionally as a result of geophagy or pica (Eshed *et al.*, 2006; Deter, 2009). Åberg *et al.* (1998) has suggested that the grit from the milling process may have been a major contributor to human $^{87}Sr/^{86}Sr$ values, particularly during the Medieval period. As of yet no study has directly researched into the bioaccessibility of Sr from rock grit or soil once ingested.

A wide range of rock types such as basalts, granites, schists and sandstones have been used as first querns and, later, millstones to grind food. Most ancient people would have used the hardest or coarsest local rock available to them for their grinding stones, but such stones were also traded and transported. For example, the Mayen Lava querns and millstones from quarries in Germany were being imported into Britain by the Roman Period (Peacock, 2013, p.151-153) and thus have the potential to introduce non-local Sr into the diets of local people *if* they provide bioaccessible Sr and *if* that Sr is metabolised in the human gut.

The current model for the origin of Sr metabolised from the omnivore diet is that it is dominated by dietary plants rather than water or animal products (Burton & Wright, 1995; Montgomery, 2010). This is due to complex antagonisms and synergisms with other dietary components such as calcium and protein that suppress, or conversely in the case of fibre and phytate enhance, elemental Sr absorption (Montgomery, 2010). Whether ingested non-food components such as soil and rock contribute has not been explored and is rarely, if ever, taken into account in interpretations. Would ground rock from a quern or millstone, or individual minerals such as radiogenic micas, as found in the intestine of the Alpine Ice Man (Müller *et al.*, 2003), provide a substantial Sr component when ingested regularly and made bioaccessible by the strong acids of the human digestive system? And could this produce very high $^{87}Sr/^{86}Sr$ in human enamel, resulting in interpretations of false migrants, e.g. >0.720, for which no host biosphere can currently be identified in Britain?

2.Tables and Figures

Table I. Typical (i.e., Order of Magnitude) Values/Ranges of Sr and Ca Concentrations, in ppm, in Some Natural Materials, as well as Rb/Sr Ratios for Geologic Materials

Material	Sr	Ca	Rb/Sr
Geologic			
Sandstone	20	40,000	3
Low-Ca granite	100	5,000	2
Deep-sea clay	180	30,000	0.6
Syenite	200	20,000	0.6
Shale	300	20,000	0.5
High-Ca granite	440	25,000	0.3
Ultramafic rock	1	25,000	0.2
Basalt	500	75,000	0.07
Deep-sea carbonate	2000	300,000	0.005
Carbonate	600	300,000	0.005
Soils			
Soil minerals[b,d]	10–1000	24,000	
Labile soil minerals	0.2–20	1,000	
Soil moisture[d]	0.001–0.07	1–4	
Water			
Seawater	8	400	
Rivers	0.006–0.8	15	
Rain	0.001–0.4	1–100	
Snow	0.00001–0.001	0.01–0.1	
Biological			
Edible plants[c]	1–100	3,000–6,000	
Mammal (incl. human) bone[c,d]	100–1000 +	~370,000	
Mammal (incl. human) enamel[e]	50–500 +	~370,000	

Note. This is a rough guide, as specific values can be highly variable. Approximated after Capo *et al*. (1998), with additions from [a]Aubert *et al*. (2002), [b]Bashkin (2002), [c]Burton *et al*. (1999), [d]Elias *et al*. (1982), and [e]Kohn *et al*. (1999).

Figure 2.1. Table 1 in Bentley (2006, p.140), which compares the Sr and Ca concentrations of natural materials.

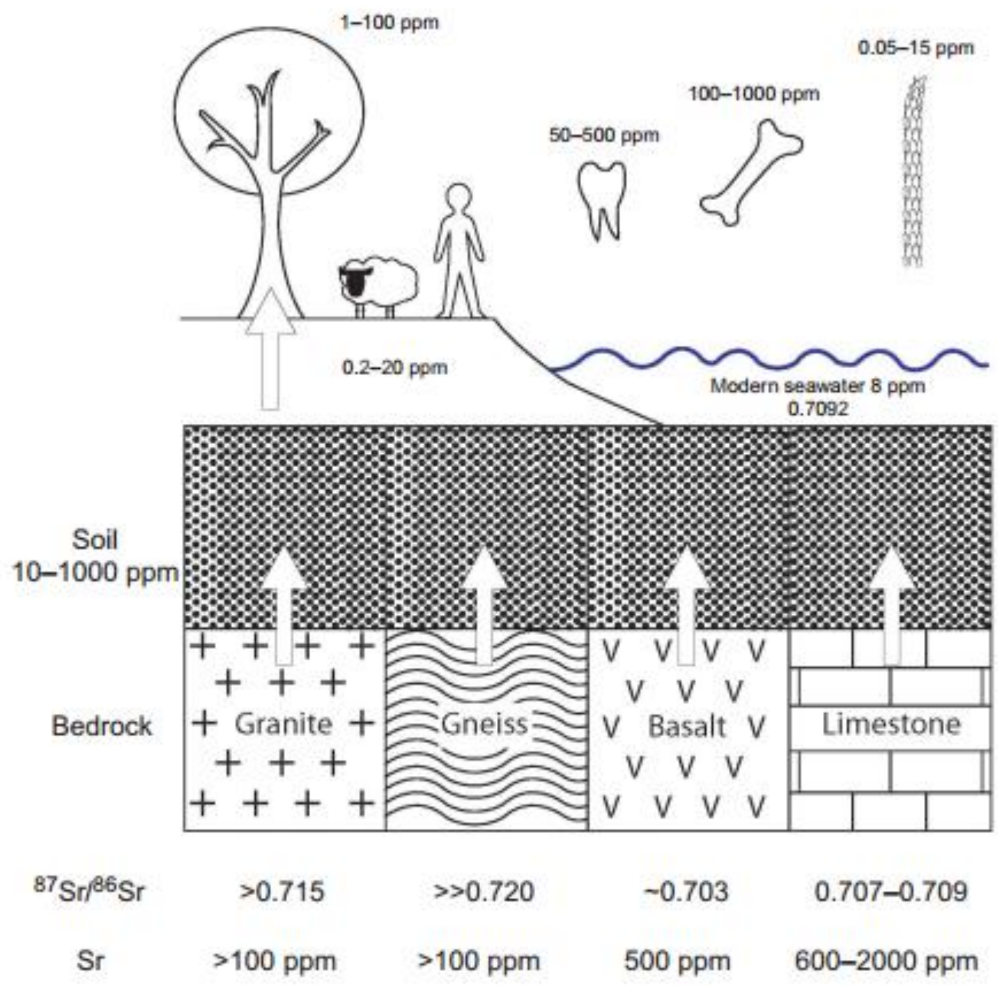


Figure 1. Diagram illustrating the strontium path from the geological strata to the human/animal hair (Frei 2010).

Figure 2.2. Figure 1 in Frei (2012, p.114), which displays the path Sr-isotopes can take from bedrock to human or animal, along with the approximate Sr concentrations (ppm).

Table 2.1. All the biosphere $^{87}Sr/^{86}Sr$ >0.714 from across Britain, along with sample code and number, location description, longitude and latitude and dominant bedrock lithology (Evans *et al.,* 2009; 2010; Chenery *et al.,* 2010; Boulton, 2011; Snoeck *et al.,* 2016; Evans, *pers.com.*). Not including the ground water (n=18) and stream water (n=3) samples on the Lower Palaeozoic mudstones and shales of the Plynlimon catchment in central Wales, as no coordinate data were available (Shand *et al.,* 2007).

Sample	Sample type	Location	$^{87}Sr/^{86}Sr$	Bedrock Lithology	Longitude	Latitude
EBP-48	Plant	Cairngorm, Etive & Angus granites, Scotland	0.72660	Granite	-3.6870	57.1640
EBP-15	Plant	County line between Moray and Aberdeenshire, Scotland (Proterozoic hotspot)	0.72513	Schist	-2.6989	57.5370
HARW-1	Water	Outer Hebrides, Scotland	0.72335	Gneiss	-6.8518	57.8566
EBP-41	Plant	Perth and Kinross, Scotland (Proterozoic hotspot)	0.72093	Schist	-3.6230	56.5880
JMW 23	Water	Moray (Chapeltown), Scotland (Proterozoic hotspot)	0.72065	Schist	-3.2550	57.2700
Skye 33p	Plant	Isle of Skye, Scotland	0.71996	Limestone	-5.9337	57.2264
I95 Shrubs	Plant	Near Dundalk, Ireland	0.71950	Granite	-6.2704	54.4992
EBP-47	Water	Cairngorm, Etive & Angus granites, Scotland	0.71937	Granite	-3.6870	57.1642

Sample	Sample type	Location	$^{87}Sr/^{86}Sr$	Bedrock Lithology	Longitude	Latitude
HIGH-02	Plant	Southern Loch Shin, Scotland	0.71930	Granulite	-4.4197	57.9276
SN1	Bone	Cairngorm, Etive & Angus granites, Scotland	0.71925	Granite	-2.8720	56.8990
Skye 36p	Plant	Isle of Skye, Scotland	0.71863	Lias	-6.0264	57.2193
Glensaugh	Water	Cairngorm, Etive & Angus granites, Scotland	0.71844	Granite	-2.5428	56.8952
Skye 34p	Plant	Isle of Skye, Scotland	0.71836	Limestone	-5.9462	57.2153
HARW-5	Water	Outer Hebrides, Scotland.	0.71821	Gneiss	-7.05230	57.9785
HARW-3	Water	Outer Hebrides, Scotland	0.71785	Gneiss	-6.8972	57.9384
Skye 31p	Plant	Isle of Skye, Scotland	0.71772	Basalt	-6.1620	57.2968
EBP-07	Plant	Southern Loch Shin, Scotland	0.71768	Granulite	-4.6490	57.5930
EBP-25	Water	Southern Loch Shin, Scotland	0.71738	Schist	-2.0684	57.3644

Sample	Sample type	Location	$^{87}Sr/^{86}Sr$	Bedrock Lithology	Longitude	Latitude
ARD 02	Plant	Southern Loch Shin, Scotland	0.71727	Granulite	-4.6807	57.2115
Skye 25p	Plant	Isle of Skye, Scotland	0.71668	Basalt	-6.3317	57.5035
HIGH-03	Plant	Southern Loch Shin, Scotland	0.71675	Granulite	-4.7335	57.9679
EBP-46a	Plant	Cairngorm, Etive & Angus granites, Scotland	0.71672	Granite	-3.6580	57.1469
EBP-04	Water	Southern Loch Shin, Scotland	0.71667	Gneiss	-5.3547	57.4670
Skye 30p	Plant	Isle of Skye, Scotland	0.71647	Basalt	-6.1875	57.3057
I94 Shrubs	Plant	Newry, Mourne and Down, Northern Ireland	0.71642	Granite	-6.7610	54.1899
G-V-026	Plant	Malvern Hills, England	0.71622	Gneiss	-2.3513	52.0302
ARD 15	Plant	Cairngorm, Etive & Angus granites, Scotland	0.71619	Granite	-4.8380	56.4540
Aberd-2	Water	Cairngorm, Etive & Angus granites, Scotland	0.71571	Granite	-3.7711	57.1351

Sample	Sample type	Location	$^{87}Sr/^{86}Sr$	Bedrock Lithology	Longitude	Latitude
Aberd-4	Water	Cairngorm, Etive & Angus granites, Scotland	0.71568	Granite	-3.7950	57.1159
USK-04	Plant	Hell's Mouth, Powys, Wales	0.71550	Mudstone	-3.3001	52.0703
GP -1	Bone	Cairngorm, Etive & Angus granites, Scotland	0.71547	Granite	-2.8720	56.8990
G-V-023	Plant	Malvern Hills, England	0.71546	Mudstone	-2.2232	52.0028
S-WALES 02	Plant	Malvern Hills, England	0.71518	Gneiss	-2.3474	52.0644
JMPD_08	Plant	Derbyshire, England	0.71514	Gritstone	-1.5664	53.0979
G-V-030	Plant	Malvern Hills, England	0.71508	Mudstone	-2.3622	52.0274
621936	Plant	South Lanarkshire, Scotland	0.71478	Mudstone	-3.6129	55.5077
FISH-4	Plant	Cambrian Mountains, Wales.	0.71467	Mudstone	-3.6229	52.408
JMW 18	Water	Cairngorm, Etive & Angus granites, Scotland	0.71463	Granite	-3.0000	57.0577

Sample	Sample type	Location	$^{87}Sr/^{86}Sr$	Bedrock Lithology	Longitude	Latitude
EBP-49	Plant	Cairngorm, Etive & Angus granites, Scotland	0.71463	Granite	-3.8190	57.1762
A08-L Shrubs	Plant	Derry and Strabane, Northern Ireland	0.71433	Schist	-7.4177	54.6706
G-V-024	Plant	Malvern Hills, England	0.71418	Mudstone	-2.3234	52.0273
I88 Shrubs	Plant	Causeway Coast and Glens, Northern Ireland	0.71402	Schist	-6.1099	55.1202

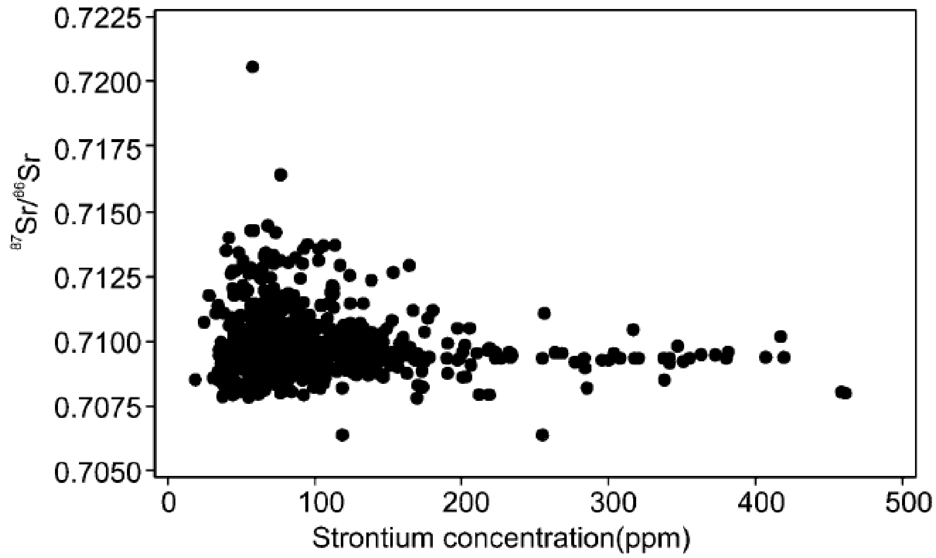


Fig. 2 A scatter diagram of strontium concentrations (ppm) plotted against $^{87}Sr/^{86}Sr$ isotope ratio for all British burials given in Appendix 1 (see ESI)†.

Figure 2.3. Figure 2 in Evans *et al.* (2012, p.756), which displays all the human Sr-isotope data currently available up to 2012 for Britain (n=614), including those deemed not to be of British origin.

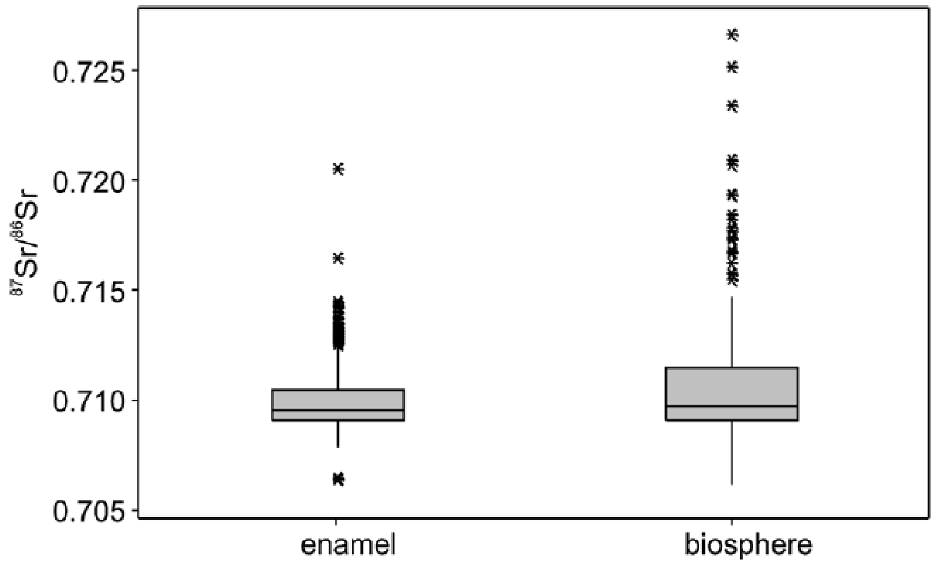


Fig. 3 Boxplot comparison of the strontium isotope composition of tooth enamel from Britain compared with biosphere data from Britain.

Figure 2.4. Figure 3 in Evans *et al.* (2012, p.756), which shows a comparison of the human vs. biosphere $^{87}Sr/^{86}Sr$ data available since 2012 in Britain, including humans deemed not to be of British origin.

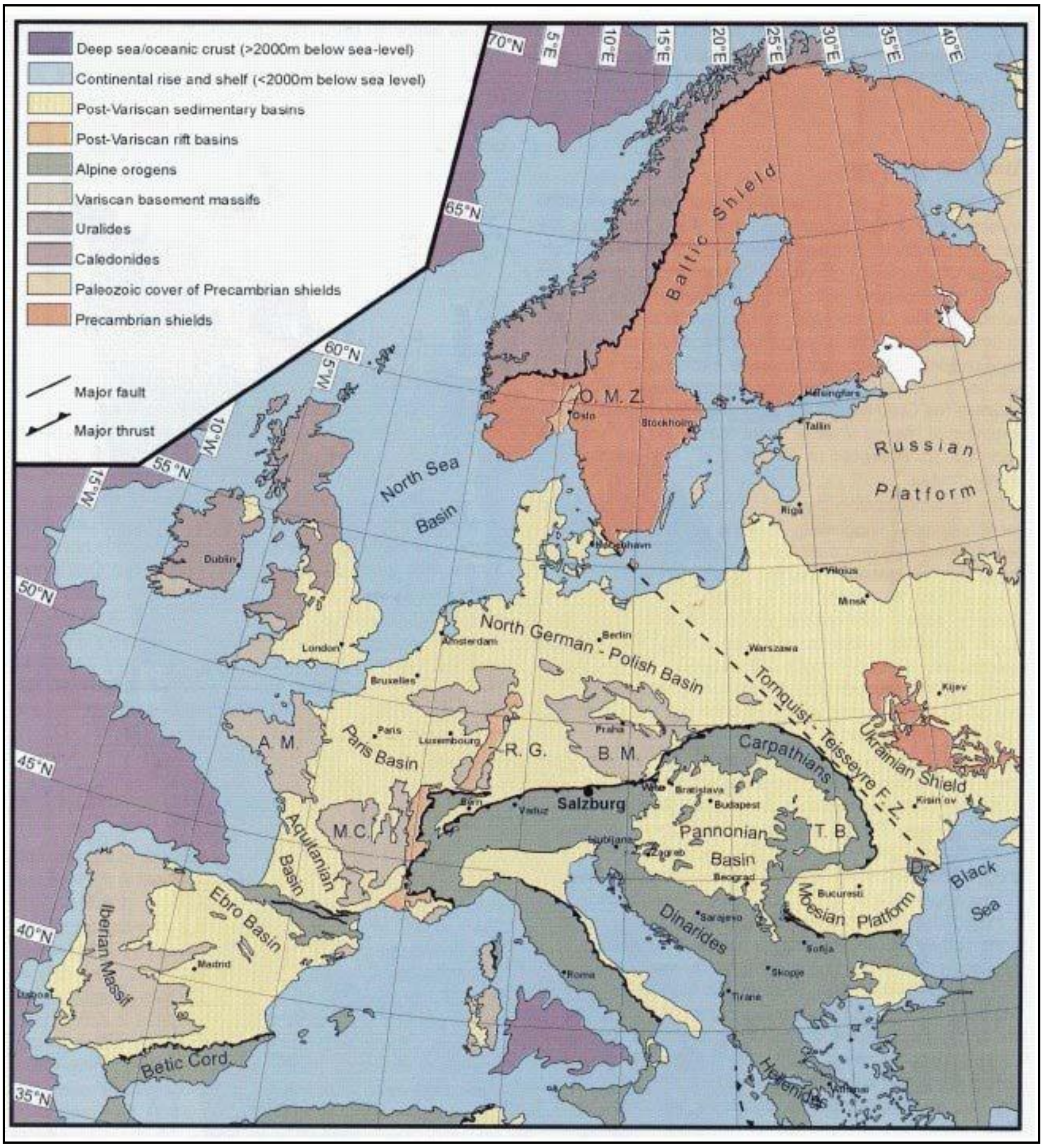


Figure 2.5. Figure 1 in Neubauer (2009), which displays a simplified geological map of Europe showing the main orogenic systems: A.M. - Armorican massif; B.M. – Bohemian massif; F.Z. – fault zone; M.C. - French Massif Central; O.M.Z. – Oslo-Mjösen Zone; R.G. – Rhine graben; T.B. –Transylvanian basin.

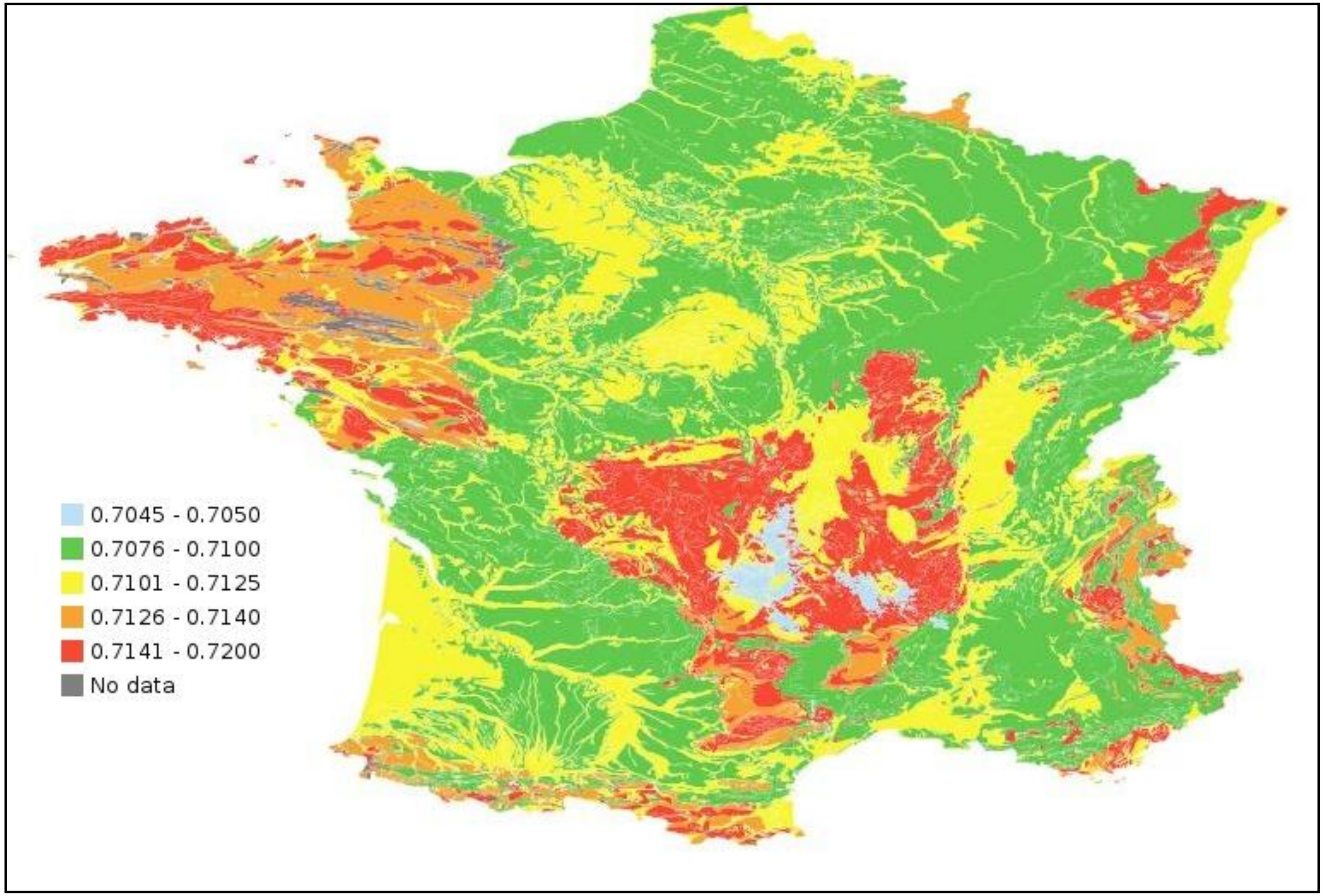


Figure 2.6. From the IRHUM database website (http://80.69.77.150/layers/geonode:sr_isotopepackages_france#more), uploaded in 2015. Displays the biosphere Sr-isotopes packages of France assigned the biosphere $^{87}Sr/^{86}Sr$ data in Willmes *et al.* (2014).

3. Materials and Methods

Plants were the main environmental samples collected to characterize the Sr-isotope biosphere in this thesis, particularly the collection of foliage from a variety of trees and large shrubs (identified as being larger than ~2m). The reason this material was collected is discussed in section 3.1. The areas of geological interest within Britain that may be able to produce radiogenic Sr-isotope biospheres are outlined in section 3.2, along with further details on the geochemical surveys (fieldwork), as well as the method of mixing different plants to create one analytical sample, which was used extensively in this thesis. The chemical preparation and column chemistry (ion exchange chromatography) of the plant samples for Sr-isotope analysis by Thermal Ionisation Mass Spectrometry (TIMS) are outlined in section 3.3. This section also outlines quality control measures and procedural reproducibility by using the NIST Standard Reference Material 1515 (Apple Leaves), which is a homogenized bulk vegetation sample with a fully certified Sr concentration. The $^{87}Sr/^{86}Sr$ results of the plants collected in each study area (see Figure 1.1 in chapter 1) are reported within each of the proceeding chapters (4, 5, 6 and 7).

3.1. Material proxies of the Sr-isotope biosphere

Most proxies used to define a local Sr-isotope biosphere are intermediates within the biosphere system, often soils, water (from rivers, streams and lakes), plants and animals. Natural materials from all of these proxies were used to create the Sr-isotope packages seen in the preliminary Sr-isotope biosphere map of Britain by Evans *et al.* (2010),with plants being the most dominant sample type used. Water from rivers, soils and plants can all be easily sampled during geochemical surveys. However, animals require the collection of bone or teeth (for dentine and enamel) which may not always be available during geochemical surveys or require consent before collection. Each proxy (whether the material collected is modern or archaeological) comes with its own set of advantages and disadvantages. These have been summarised in an adapted table by Warham (2011, p.30) during his second chapter of his doctoral thesis (Warham adapted his table from Evans & Tatham, 2004) and is displayed in Table 3.1.

Plant samples were the primary proxy collected in this thesis. Their advantages are that they are a direct measurement of the biosphere, they are of known provenance and they very rarely have any ethical consent issues or specialised permission to access material (Table 3.1: Evans & Tatham, 2004; Bentley, 2006; Warham 2011, p.28-34). They have also been shown to consistently average the local biosphere $^{87}Sr/^{86}Sr$ accessible to them from soil and water (Sillen *et al.,* 1998; Price *et al.,* 2002; Poszwa *et al.,* 2002; 2004; Bentley, 2006, p.148-150; Warham, 2011, p.70-96) and are the dominant dietary input of Sr in animals and humans (Burton & Wright, 1995; Montgomery, 2010). Overall human $^{87}Sr/^{86}Sr$ and plant $^{87}Sr/^{86}Sr$ have a strong link to one another. Their practical disadvantages are also being improved at a better rate than some of the other proxy types. Plants have been known to have challenging chemical preparation for Sr-isotope analysis due to their complex organic structures which can lead to a range of chromatographic interferences (Rosner, 2010; Evans *et al.,* 2010) and problems when analysed by TIMS (such as early emission, weak or unstable beam, catastrophic beam collapse; Warham, 2011, p.37). However, the development of microwave assisted digestion by Warham (2011, p.42) has resulted in an efficient method of complete digestion of the plant organic structure providing much better and reliable Sr yields. This microwave assisted digestion was also preliminarily seen in Evans *et al.,* (2010). The above problems have been dramatically reduced because of this improved method, as well as the time taken to chemically prepare the samples ready for analysis by TIMS.

The main disadvantage of plants during geochemical surveys is that they can be point-samples, determined by the scale and character of nutrient uptake of that particular plant chosen. Often the $^{87}Sr/^{86}Sr$ acquired from plant samples used in migration and mobility studies are from single plants. If collecting in high density, the analysis of single plants can be very useful with the conduction of statistical analysis. However, Sr-isotope analysis is expensive and often not enough samples are collected to conduct any meaningful statistical analysis. Also these $^{87}Sr/^{86}Sr$ values from single plants are often inferred to occur over large areas which can lead to misconceptions. There could be a lot of bias around that single plant sample, its nutrient uptake for example could be different than all the surrounding plants leading to a different $^{87}Sr/^{86}Sr$. This disadvantage can be improved and in section 3.2.2 the proposed method of mixing several plants into one analytical sample to lessen this point-sample bias is further discussed.

Samples of soil, water and animal remains were not collected or analysed during this thesis, but were not dismissed without reason. Soil samples were not collected mainly because they are not a direct measurement of the biosphere, but are instead a measurement of what can potentially be released into the biosphere (Evans & Tatham, 2004; Evans *et al.,* 2010, supp material). They can also display a great deal of variability, which does not always resemble the $^{87}Sr/^{86}Sr$ of water or plants samples from the same location, often being off-set towards more radiogenic values (Sillen *et al.,* 1998; Poszwa *et al.,* 2002; Warham, 2011, p.70-96, Willmes *et al.,* 2014). This variability can be caused by the natural variations of $^{87}Sr/^{86}Sr$ with soil depth, where normally contributions from atmospheric Sr sources decrease, while Sr contributions from the bedrock increase with depth (Capo *et al.,* 1998, Vitousek *et al.,* 1999; Probst *et al.,* 2000; Pourcelot *et al.,* 2008; Chadwick *et al.,* 2009). The $^{87}Sr/^{86}Sr$ of soil samples can also depend on the leaching process used during chemical analysis (Evans *et al.,* 2010).

The collection of water samples was considered more highly than soil samples, but ultimately no water samples were collected in this thesis. Surface water from rivers can provide a good average of the $^{87}Sr/^{86}Sr$ over their catchment area. However, this can be effected by seasonality and the amount of rainfall, as well as differing weathering rates and a bias towards the $^{87}Sr/^{86}Sr$ in minerals that are more soluble (Table 3.1: Shand *et al.,* 2009; Evans *et al.,* 2010; Warham, 2011, p.28-31). Occasionally, this can result in a river displaying $^{87}Sr/^{86}Sr$ typical of their upper catchment rather than the surrounding area of their collection location. Other surface water, like lake water has the addition of equilibrating with their lakebed, which can, depending on the bedrock geology, result in a more radiogenic value than seen in plants (Evans *et al.,* 2010). Water $^{87}Sr/^{86}Sr$ and plant $^{87}Sr/^{86}Sr$ in Warham (2011, p.82, 89) have shown very similar values, but plants outweighed water in terms of their advantages (Table 3.1) and because of their connection to the food-chain and being the dominant dietary input of Sr in animals and humans (Burton & Wright, 1995; Montgomery, 2010). Water samples can be a useful proxy to collect, especially for comparison with other proxy samples, but ultimately in this thesis they were not collected. This came down to the fact that considering the amount of geochemical surveys conducted, plants were far easier to collect and guaranteed to be at any location visited. During geochemical surveys water samples require more preparation before hand, in terms of location planning and different equipment (centrifuge tubes and methods of leak prevention), than plants. Water samples also benefit from being stored in cool conditions after collection to slow down any biotic activity (advised below 4^{o}C but above freezing: Grimstead *et al.,* 2017, p.6), while plant samples benefit from being air dried (still in their sample bags if need be) once collected.

Animal remains, whether modern or archaeological, have the potential to display even more consistent averages of $^{87}Sr/^{86}Sr$ accessible to them through the biosphere compared to plant samples, as they are further up the food chain (resulting in an averaging effect; Blum *et al.* 2000; Price *et al.,* 2002; Bentley, 2006, p.154-155). For archaeologically contexts choosing to analyse certain species similar to humans, such as pigs, means they can be used as predictions for human $^{87}Sr/^{86}Sr$ (Bentley, 2006, p.158; Evans *et al.,* 2010). However, with reference to Table 3.1, the collection and analysis of animal remains have many disadvantages, namely the uncertainties in provenance and feeding range for wild animals and the importance of non-local food sources for both wild and domestic animals. Further problems can also arise when dealing with archaeological animal remains, such as issues with teeth mineralization and their availability dependant on burial conditions and preservation (leading to bias in favour of non-acidic burial environments; Evans *et al.,* 2010, supp material). The collection of modern domestic animals or archaeological animal remains were not considered due to the large number and size of the study areas and the consent that may have been needed. However, the natural remains of wild animals (in skeletal form) were looked for during geochemical surveys. These would have been collected if they were easily available, unfortunately no such skeletal remains were found. The collection of snails were not considered due their $^{87}Sr/^{86}Sr$ being more reflective of the rainwater value (~0.7092) in Britain, instead of an average of the biosphere obtained through their ingestion of plants, regardless of the substrate they are taken from (Evans *et al.,* 2010).

3.2. Geochemical Surveys and Mixed Plant Samples

3.2.1. Areas of geological interest in Britain for Sr-isotope biospheres with values >0.714.

It has been shown in chapter 2, section 2.4 that the best areas within Britain that may produce radiogenic $^{87}Sr/^{86}Sr$ in the biosphere need to be situated on bedrock that contain felsic igneous lithologies, such as granite, rhyolite, etc. (or their metamorphic equivalents), and they generally need to be old, e.g. Precambrian to late Palaeozoic in age. Targeting any igneous area dating from the Precambrian to late Palaeozoic (mainly Ordovician to Silurian) was prioritized, and ideally the larger the bedrock outcrop the better.

Within England and Wales the Precambrian inliers occur within Charnwood Forest, the Malvern Hills, within Shropshire and along the Welsh border, the outskirts of Snowdonia, along coastline of Anglesey and Llín (the Lleyn Peninsula) and the south-west tip of Wales (Pharaoh & Carney, 2000). Figure 3.1 is from Pharaoh & Carney (2000, p.3) and shows where the main Precambrian inliers are situated in England and Wales. They all contain some form of felsic igneous lithology within their sequence stratigraphy. At present there is not much Sr-isotope biosphere data available from the majority of these Precambrian inliers in England, apart from the Malvern Hills where Chenery *et al.* (2010) and Evans (unpublished results; pers.com.) have reported plant $^{87}Sr/^{86}Sr$ between 0.709 - 0.716. In Wales, there is more biosphere data available from the Precambrian inliers. Around Anglesey the biosphere $^{87}Sr/^{86}Sr$ = 0.7097 ±0.0007 (n=8, 1SD: Evans *et al.,* 2010), while from the south-west of Wales (towards Newport) plant $^{87}Sr/^{86}Sr$ = 0.7091 - 0.7125 (n=15: Evans *et al*., 2010; Evans, unpublished results; pers.com.). Evans *et al.* (2010) note that in the case of Anglesey, despite the underlying bedrock dating to the Neoproterozoic (part of the Precambrian), the values from the biosphere are close to the marine value of c.0.7092, due to the proximity of the coast and the high level of rainfall western Britain receives. A similar yet less severe situation occurs to the south-west of Wales, where the biosphere values become more radiogenic with increasing distance from the coast. Still no values >0.714 have been recorded above the Precambrian bedrock in Wales.

Further sampling from the Precambrian bedrock of Anglesey and south-west of Wales was not considered due to the marine effect described above, along with no biosphere samples currently producing $^{87}Sr/^{86}Sr$ >0.714. Instead, the other Precambrian inliers found in England were focused on, being further inland where coastal sea-spray and lower rainfall should not contribute as much atmospheric Sr to the biosphere and hence not produce values c.0.7092 (Veizer, 1989, p.142) unless the bedrock releases such values to the biosphere. In total, the Precambrian inliers sampled from in this thesis are as follows: the Charnian Supergroup in Charnwood Forest (Leicestershire); the Caldecote Volcanic Formation near the town of Nuneaton (Warwickshire); the Malvern Igneous Complex which forms the Malvern Hills (Herefordshire); the Stanner-Hanter Complex near Kington (Herefordshire); the Longmyndian Supergroup and Uriconian Group around the town of Church Stretton (Shropshire); the Uriconian Group at the Wrekin (Shropshire). The last three lie along the Welsh Borderland Fault System and all can be seen in Figure 3.1 (Pharaoh & Carney, 2000). Each of these study areas are presented individually in chapter 4.

The Ordovician to Silurian igneous intrusions of the Lake District, Cumbria, were also investigated as no biosphere data from around this area had currently been collected. The Lake District has large granitic intrusions (larger than many of the Precambrian inliers within England) as well as extensive lavas and tuffs (some of which are felsic in composition) and so had potential to produced radiogenic biospheres with values >0.714. At some points, the coast was approximately 4km west of the granitic intrusions, therefore sea-spray and precipitation were expected to influence the biosphere $^{87}Sr/^{86}Sr$, but gradually lessen moving inland. Again, this study area can be found in chapter 4.

From Evans *et al.* (2010) it is known that certain areas in Scotland can produce radiogenic values >0.714 (chapter 2, section 2.3.1). These areas include the Siluro-Devonian granites of the Cairngorms mountain range, the Precambrian Dalradian metasedimentary rocks of the Central Highlands and the Northwest Highlands, and the Precambrian Lewisian gneisses. However, the Sr-isotope biosphere data was not collected as extensively in Scotland compared to England and Wales (Evans *et al*., 2010). More data would be beneficial to further define the maximum $^{87}Sr/^{86}Sr$ that can be produced consistently from the radiogenic biospheres identified in Scotland. To achieve this a transect was designed, starting from Blairgowrie in the county of Perth and travelled up to Grantown-on-Spey in the county of Moray (approximately 144km), which covered a variety of bedrock geology, notably the Silurian granites of the Cairngorms mountain range and the Precambrian Dalradian metasedimentary rocks of the Central Highlands. Around the village Chapeltown in the county of Moray and the area to the north of the Cairngorms mountain range, around Glenmore (which is near to Aviemore) were also focused on to see if radiogenic values can be successfully repeated and specifically grouped into smaller magnitudes. Most isotope packages in Evans *et al.* (2010) were grouped in magnitudes of 0.001 until values >0.713, where the packages are spilt into 0.713-0.720 and >0.720. Further sampling from Scotland (as well as England) could potentially lead to further separation of the packages for radiogenic values >0.713. All the study areas from Scotland can be seen in Figure 1.3 in chapter 1 and are reported in chapter 5.

3.2.2. Geochemical Survey Methods

All the plant samples in the proceeding chapters, apart from within the Charnwood Forest study area (section 4.1 in chapter 4), have been a mixture of different plants collected over a given area. The study from the Malvern Hills (section 4.2 in chapter 4) was the first that fully participated in the collection of different plants with the intention of mixing them to produce one single analytical sample. In this study area one analytical sample equates to the mixture of plant material from at least three different locations over 1km^2. At each location a large selection of plant foliage was collected from one particularly species (but could cover several trees or large shrubs if available). For the remainder of the study areas in chapter 4, 5, 6 and 7, plant material was collected from three locations within a 500m radius to make one analytical sample. The area in which the plants were collected per analytical sample decreased from conducting the Malvern Hills study to the proceeding studies because several geochemical surveys were conducted, with some covering large distances, leading to the amount of fieldwork required becoming excessive under the time constraints.

The locations for collecting the plant samples were not chosen at random. They covered a variety of the bedrock geology present within each study area, so as not to cause bias of only preselecting the rocks deemed to have high $^{87}Sr/^{86}Sr$. They also covered variety of different land uses (villages/towns, agricultural land, heath or common land, etc.), although a conscious effect was made not to collect any plants directly within agricultural land, only surrounding them. Although the locations could have benefitted from being collected from random places, calculated without human bias, this was not possible for several reasons. Firstly, a lot of the surveys covered large areas (>400km^2) with a variety of possible access restrictions (private roads or land, extensive water sources, steep relief, unavoidable dangers, etc.) and safety had to come first. There were also time restrictions to complete the surveys. Consequently, locations had to be chosen that were easy to access by car and foot in a realtively small amount of time. The use of google maps aided in selecting suitable locations, but once in the field some locations changed because of unforseen circumstances, such as unexpected access issues and unsuitable or dangerous parking options.

Britain has a temperate environment with a variety of vegetation available all year round, but more so through spring to late autumn when deciduous plants have their foliage. Foliage is easy to collect, not needing specialist training, even in bulk, and when compared to wood requires less protracted preparation (Warham, 2011, p.144-150, 232). Therefore geochemical surveys were mainly conducted during the spring to early autumn of each year (April - early October).

The type of plants chosen were also considered and it was decided that trees or large shrubs were preferential over low-lying, shallow rooted plants for defining the maximum biosphere $^{87}Sr/^{86}Sr$ available in Britain. Trees and large shrubs are not consumed as regularly or to as high proportions as the likes of grasses and crops by domestic animals and humans, but they do have deeper penetrating roots and so can utilise deeper water and nutrient sources in the soil. They can cover much larger area and are not as affected by the contributions of Sr from atmospheric depositions, often being much closer to the $^{87}Sr/^{86}Sr$ of the bedrock (Maurer *et al.,* 2012; Hartman & Richards, 2014). Low-lying, shallow rooted plants like grasses and crops are quite versatile, found in a variety of environmental niches and can make up a significant proportion of the animals and human diets (both modern times and the past). Nevertheless, there can be a great difference in the scale and character of nutrient uptake between the likes of a grass or a crop compared to a tree or large shrub. Grasses on average have 44% of their roots concentrated in the first 10cm of a soil, compared to 21% in shrubs (Jackson *et al.,* 1996 in Hartman & Richards, 2014). This first 10cm of the soil can be easily dominated by atmospheric Sr (Capo *et al.,* 1998, Vitousek *et al.,* 1999; Probst *et al.,* 2000; Pourcelot *et al.,* 2008; Chadwick *et al.,* 2009), particularly in areas of high rainfall, such as the western coast of Britain. Therefore, shallow rooted plants are more likely to be affected by the atmospheric Sr in soils and overall tend to produce less radiogenic $^{87}Sr/^{86}Sr$ values compared to trees and large shrubs in the same area (Maurer *et al.,* 2012; Hartman & Richards, 2014). The analysis of tree and large shrub samples potentially represent the maximum $^{87}Sr/^{86}Sr$ bioaccessible to the food-chain in a given area, even if they are not consumed as regularly by animals and humans.

Trees and large shrubs are also a better choice if having to sample from or around agricultural land as they should provide $^{87}Sr/^{86}Sr$ values that average all Sr-isotope inputs in their local vicinity and not just the methods of modern human activity. Grasses and crops on agricultural land will likely have the added addition of fertilisers to consider and other farming practices such as intensive irrigation (which may also lead to saturated soils). Although methods of using fertilisers and irrigation existed in the past they were not equal to modern day agricultural practices and did not cover the same volume of land as seen in Britain today (up to 75%: Khan *et al.,* 2011). Ideally, if wanting to reconstruct more accurate archaeological biospheres, plants from within agricultural land should be avoided due to possible changes in $^{87}Sr/^{86}Sr$ values caused by modern day human activity (Maurer *et al.,* 2012; Crowley *et al.*, 2015). However, this is not always possible due to the large percentage of agricultural land that covers Britain today and so sampling trees or large shrubs on the outskirts of agricultural land is considered the best compromise.

Finally, grasses and low-lying crops can easily fall victim to mud-splash resulting in soil contamination which can result in a $^{87}Sr/^{86}Sr$ reflective of the mud-splash and not the plant during chemical analysis (Evans, *pers.com.*). Trees and large shrubs with their leaves elevated from the ground can avoid this mud-splash issue. They are more susceptible to being coated in surface deposits transported by the wind (the likes of dust, loess, pollution or a combination of all), but considering the study by Warham (2011, p.144-150) described previously, this dust will make no significant contribution to the bulk $^{87}Sr/^{86}Sr$ of the plant leaves. Where possible, plants were not collected if they suffered from mud-splash or excessive surface deposits.

Each plant collected was sealed in a labelled brown paper envelope or kraft paper sample bag and allowed to dry naturally before being artificially mixed (see section 3.2.3 below). Occasionally, low-lying, shallow rooted plants were selected if large shrubs or trees were inaccessible (e.g. deemed dangerous to collect, on land that needed permission to access, etc.) or not present. These are noted down in the field-notes for each study area, along with the identification of the plants chosen, all of which can be viewed in the Appendix 2. The plants were identified using guides such as 'the Observer's Book of Trees and Shrubs of the British Isles' (Stokoe, no publication date), 'Trees Collins Gem Guides' (More & Fitter, 1980) and information on the Woodland Trust website (https://www.woodlandtrust.org.uk/visiting-woods/trees-woods-and-wildlife/british-trees/). Land use and any other features, such as water sources, exposed rocks, etc., were also noted in the field-notes, in case they are needed during the interpretations of the plant $^{87}Sr/^{86}Sr$ data in the proceeding chapters.

3.2.3. Mixed Plant Samples

Common practice in migration and mobility studies to obtain $^{87}Sr/^{86}Sr$ for the local biosphere typically requires multiple sampling and analysis of individual plants across a given area, usually kilometres. These values are then averaged to obtain a mean $^{87}Sr/^{86}Sr$. For example, Hoppe *et al.* (1999) averaged a minimum four plant samples per site during their study of migratory mammoths and mastodons. This process is not only time consuming but rather costly. However, the artificial pre-mixing of individual plant samples prior to analysis is not commonly practiced.

The proposed artificial mixing of several singular plant samples over a certain area to create one mixed analytical sample could potentially reduce the main disadvantage of using plant samples as a proxy for biosphere $^{87}Sr/^{86}Sr$; that being a point-sample (see Table 3.1). Collecting mixed plant samples could also lead to a reduction in the analytical burden and costs, as larger areas could be covered during geochemical surveys with fewer samples to analyse. The main advantage to this though is that the mixing is presumably imitating the normal mixing of food sources and potential Sr-isotope inputs that a local animal or human undergoes when consuming in its natural habitat (initially based on the start of the food chain, e.g. plants). The dataset is effectively being artificially 'smoothed' in a similar manner to what would happen in the natural environment; that is a weighted bias towards the most dominant $^{87}Sr/^{86}Sr$ value in the local biosphere being displayed. Therefore the analysis of mixed plant samples will likely characterise the plant $^{87}Sr/^{86}Sr$ being consumed and averaged within local animals and humans. A higher density of plant samples will be needed during geochemical surveys and there will still likely be unavoidable biases during collection, but overall this method should lead to better interpretations of the 'local' Sr-isotope biosphere during mobility and provenance studies.

The process involved the collection of several plant samples over a given area (the numbers are outlined above in section 3.2.3) and mixing them artificially before any chemical treatment. This mixing was achieved by the use of a mini chopper (Russell Hobbs) in the Archaeological Environmental Processing Laboratory at Durham University. The Archaeological Pollen and Isotopic Analysis Lab was not used because the plant samples being prepared could lead to the contamination of bones and teeth also being prepared for Sr-isotope analysis by other staff or students. Approximately 1g from each individual plant collected over a given area were weighed and blended via the mini chopper before being deposited in a newly labelled brown paper envelope or kraft sample bag. This typically equated to at least 3g of mixed plants being present for each analytical sample, which is over 10 times the amount required for chemical preparation and analysis by TIMS. It also homogenises the mixed plants resulting in a flaky texture like the 'tea-leaf' consistency described in Evans *et al*. (2010) and allows for a large surface area for reagents to react during chemical preparation (section 3.3.1). Although the NIST Standard Reference Material 1515 (Apples Leaves) was in a powdered form, further homogenising of the mixed plant samples to a powdered consistency (using the likes of a cryogenic mill) was deemed unnecessary, as previous data from plant samples at the NIGL have shown no meaningful discrepancy between plants analysed in powdered or flaky form (Evan *et al.,* 2010; Evans, *pers. com*).

Between each analytical sample being prepared, the mini chopper was washed with 900mL of de-ionised water 3 times (all internal parts were submerged at some point in this process), allowed to dry for up to 15 minutes and fully wiped down with Kimtech Science lint-free precision wipes. This was done to reduce the effects of cross-contamination while still maintaining some speed to the mixing procedure. Due to the large amount of plant material being mixed, it was assumed that the stainless steel blades would not make any significant contribution to the Sr component of the mixed samples.

3.3. Chemical Preparation and Analytical Methods

All measurements of plant $^{87}Sr/^{86}Sr$ were obtained from the use of Thermal Ionisation Mass Spectrometry (TIMS; section 3.3.3) via a Thermo Triton multi-collector mass spectrometer , which was housed within the clean lab facilities at the NERC Isotope Geosciences Laboratory (NIGL) at the British Geological Survey, Keyworth, Nottingham. The chemical preparation, including column chemistry (section 3.3.1 and 3.3.2), needed to create appropriate Sr samples for analysis by TIMS from plant samples was also conducted within the clean lab facilities at the NIGL and involved the use of ultrapure reagents and pre-cleaned acid-leached Savillex© vessels and MARS microwave dissolution tubes (made of Teflon®). The cleaning and preparation of Savillex© vessels and MARS microwave dissolution tubes, as well as cation exchange resin columns are outlined in Appendix 3.

3.3.1. Chemical Preparation; microwave-assisted method

The chemical preparation of plant samples for Sr-isotope analysis is based on the microwave-assisted method of vegetation digestion developed by Warham (2011, p.42), which was preliminary used in Evans *et al.* (2010). This method prepares the plant samples ready to be converted into a solution for extracting Sr through ion chromatography by using cation exchange resin columns (section 3.3.2 below).

Approximately 200mg of each plant sample was transferred into clean, labelled microwave dissolution tubes and 2mL of 8M nitric acid(HNO_3) added to each. These were transferred to a hotplate (60^{o}C), with lids screwed on loosely and allowed to react overnight (approximately 12 hours). The samples were removed, allowed to cool, then 5mL of 8M HNO_3 and 100uL of hydrogen peroxide (H_2O_2) were added respectively. The lids of each microwave dissolution tubes were tighten and transferred into the microwave system (CEM MARS Xpress Xtraction) and microwaved at 175^{o}C for 20 minutes using a slow ramp up. It was optional before this stage to return samples onto the hotplate (60^{o}C) for up to one hour to help start the reaction of the reagents (judgements was usually made based on the plant type being chemically digested). Once the microwave system had completed and cooled, 500uL of $H_2O_2$was added to each and samples returned to hotplate ($60^{o}C$) overnight (approximately 12 hours) with lids screwed on loosely. New, clean Savillex© beakers were labelled and the samples decanted into them. These were returned to the hotplate ($60^{o}C$) and allowed to dry down (approximately three to four hours). If organics were still present in the samples at this point, a further 2mLof 8M HNO_3 and 100uLof H_2O_2 was added respectively and returned to the hotplate to dry down ($60^{o}C$) for approximately one to two hours.

3.3.2. Column chemistry; Ion Chromography

The dried down samples from section 3.3.1 above were converted into a solution, from which Sr can be separated by using cation exchange chromatography (Dickin, 1995, p.452). Once completed, the samples should be in a state where they were able to be loaded onto the Thermo Triton multi-collector mass spectrometer and analysed by TIMS (section 3.3.3 below). Two types of calibrated cation exhange resins were used during this thesis: Dowex AG 50W-X8 and Sr-SPEC.

3.3.2.1. Dowex AG 50W-X8 Resin Columns

The majority of the plant samples prepared for column chemistry used the Dowex AG 50W-X8 resin columns. Continuing on from section 3.3.1, the dried down samples are converted to chloride, by adding 2mL of 6M hydrochloric acid (HCl) using a measuring cylinder. These were returned to the hot plate ($60^{o}C$) for two to three hours to completely dry down. The chloride-converted samples were dissolved in 2mL 2.5M HCl and decanted into labelled centrifuge tubes, while the Savillex© beakers were cleaned ready to be used for Sr collection later (see Appendix 3, section 3.3). These were transferred into the centrifuge machine (Thermo Scientific Heraeus Labofuge 400) and ran for 10 minutes at 3000rpm. Any suspended solids in the solution that have not been separated were centrifuged further, and then 1mL of the solution was transferred to the calibrated Dowex AG 50W-X8 resin column. The remaining 1mL was saved for repeats if necessary. The Sr was eluted in the specified volume of 2.5M HCl, which was calculated depending on the calibration of the Dowex AG 50W-X8 resin. Table 3.2 displays the volumes needed to elute Sr from the resin over the period of this thesis. The elute of the waste solution (containing the ions no wanted such as Na, K, Rb, Ca, etc.) was collected in glass beakers and disposed of in an appropriate manner. The eluted Sr was collected in the cleaned Savillex© beakers and returned to hot plate (~105^{o}C) to dry down overnight.

3.3.2.2. Sr-SPEC resin columns

The Sr-SPEC resin was used in conjunction with 2mL Savilex© columns. The Sr-SPEC resin columns were only used for batch P730 (which included mixed plant samples from the Lake District and Wrekin) on the 12/10/15 as the Dowex AG 50W-X8 resin columns were unavailable. The mixed plant samples in this batch followed the same chemical preparation outlined in section 3.3.1, but then followed the proceeding method of column chemistry based on Muynck *et al.* (2009). The dried down samples were converted to nitrate by adding 1.5mL of 2M HNO_3. These samples were then decanted into labelled centrifuge tubes while the Savillex© beakers were cleaned ready to be used for Sr collection later (see Appendix 3, section 3.3). The samples were transferred into the centrifuge (Thermo Scientific Heraeus Labofuge 400) and ran for 5 minutes at 3000rpm. Any suspended solids in the solution that were not separated were centrifuged further, and , then 1mL of the solution was transferred to the calibrated Sr-Spec resin column. To elute the waste solution 0.5mL of 2M HNO_3, 1mL of 7M HNO_3 and approximately 75uL (~3 drops) of 2M HNO_3 were added respectively to each column and a glass beaker was present under each column to collect the waste solution The collected waste solution was disposed ofin an appropriate manner. The clean Savillex© beakers were placed under the columns and 2mL of 0.05M HNO_3 was added and allowed to drain. These were then transferred to the hot plate (105^{o}C) and allowed to dry down for approximately one to two hours.

3.3.3. Thermal Ionisation Mass Spectrometry (TIMS)

The Sr samples were all loaded onto out-gased single Rhenium (Re) Filaments with TaF following the method of Birck (1986). Each sample being taken up in 2uL of a TaF activator solution and loaded onto the Re filament. The loaded filaments were drid down in a HEPA-filtered fume cupboard before being placed in the Thermo Triton multi-collector mass spectrometer ready for analysis.

Typically, each analytical batch includes up to 21 samples, 3 of which are the international standard NBS 987. This allowed the data collected during the different analytical periods to be compared directly as well as allowing them to be compared between different laboratories. Samples were run using a peak jumping protocol for 10 blocks of 10 cycles. A rejection criteria was in place that allowed for up to 10% (n=10) of the measurements to be excluded from the data-set as outliers. Mass-dependant fraction of $^{87}Sr/^{86}Sr$ was corrected during each run using $^{86}Sr/^{88}Sr$ = 0.1194.

The international standard NBS 987 analysed over the period of this thesis produced a $^{87}Sr/^{86}Sr$ of 0.710254 ±0.00001 (n=146, 2SD) and can be viewed in the Appendix 3 (section 3.4). Therefore the internal precision (2SD) is ±0.00001 over the course of this .

3.3.4. Characterization of blanks and reproducibility

3.3.4.1 Procedural blanks

Procedural blanks were used to monitor the quality of reagents used, the analytical processes and laboratory proficiency. The blank controls the size of the sample that can be analysed with acceptable accuracy. The majority of the analytical batches contained at least 2 blank samples that underwent all the same chemical preparation and analytical methods of the plant samples outlined in section 3.3. These blank samples were spiked with approximately 30uL (~2 drops) solution of Oak Ridge Sr Spike to allow for calculation of absolute Sr concentration. Over the analytical period of this study the average external blank values, which included the microwave dissolution, was ca.152pg. If it is assumed that the Sr concentration in the plant samples was about 10ppm and that 0.2 grams of a sample were dissolved, this blank represents 0.00008% of the total Sr load and hence is an insignificant contribution to the overall result.

3.3.4.2. Procedural reproducibility

There are currently no external international $^{87}Sr/^{86}Sr$ biosphere standard available. At the NIGL (BGS, Keyworth) the NIST Standard Reference Material 1515 (Apple Leaves), which is a well homogenised bulk vegetation sample, has a fully certified Sr concentration (ppm: NIST, 2017) and is used for external precision monitoring. This standard material was used to validate that the chemical procedures in section 3.3.1 and 3.3.2 can be reproduced with precision and accuracy and so data collected from different dates can be compared.

The NIST SRM 1515 underwent all the same chemical preparation and analytical methods as the plant samples in section 3.3 and were spiked with approximately 100uL (~4-5 drops) solution of Oak Ridge Sr Spike to allow for calculation of absolute Sr. The results are shown in Table 3.3. The average $^{87}Sr/^{86}Sr$ = 0.71395 ±0.00005 (n=14, 2SD) for the NIST SRM 1515 and compares well to those also recorded in Warham (2011, p.44-46), with an average of 0.71394 ±0.00005 (n=20, 2SD).

The average Sr ppm of 25.2 ±3.1 (n=14, 2SD) is also similar to the certified ppm concentration of Sr= 25.1 ±1.1 (2SD) for the NIST SRM 1515 (NIST, 2017). The relative standard deviation (%2SD) of the Sr ppm in Table 3.3 is at ±12.2%, compared to ±8.8% for the certified concentration. The precision of the isotope dilution method is heavily dependent on the accuracy and precision of the sample and spike weight measurements. The slightly elevated uncertainty on the result, over the certified values, may reflect the difficulty in getting a good measurement with the static susceptible and light weight sample material.

3. Tables and Figures

Table 3.1: Taken from Warham (2011, p.30), which has been adapted from Evans & Tatham (2004, Table 1). Displays the common sample media used to characterize biosphere $^{87}Sr/^{86}Sr$ values with their main advantages and disadvantages.

Sample Medium	Biosphere Compartment	Advantages	Disadvantages
Soil-leach	Reservoir of labile strontium	● Analytical simplicity ● Known provenance	● Operationally-defined value ● Localised point-sample or artificial composite ● Vertical variation through soil Profile
Stream water	Weathering solution run-off	● Bulk measurement ● Spatial averaging ● Analytical simplicity ● Known provenance	● Biased by most soluble minerals ● Seasonal change ● Weather-related variation
Domestic Animals	Biomass	● Temporal buffering ● Biosphere measurement ● Spatial averaging ● Known provenance	● Imported feed and nutritional supplements (non-local food sources) ● Livestock management Movements
Wild animals		● Biosphere measurement ● Temporal buffering ● Spatial averaging	● Uncertain provenance ● Uncertain feeding range ● Non-local food sources and nutritional supplements ● Ethical consent
Vegetation		● Biosphere measurement ● Bulk measurement ● Temporal buffering ● Trophic position (base of food-chain) ● Known provenance	● Character of point-sample sample determined by scale and character of nutrient uptake by plant ● Challenging sample Preparation

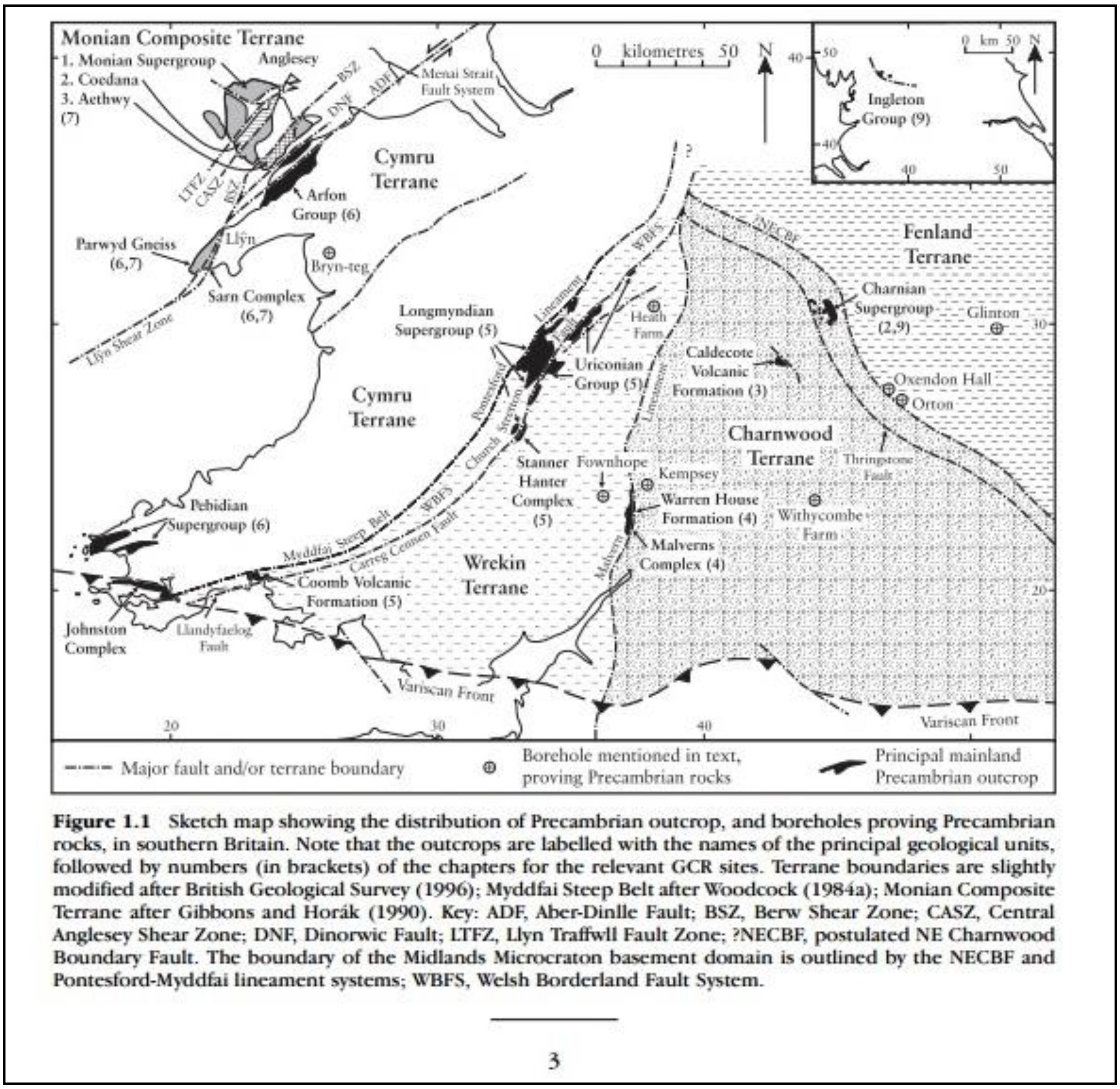


Figure 1.1 Sketch map showing the distribution of Precambrian outcrop, and boreholes proving Precambrian rocks, in southern Britain. Note that the outcrops are labelled with the names of the principal geological units, followed by numbers (in brackets) of the chapters for the relevant GCR sites. Terrane boundaries are slightly modified after British Geological Survey (1996); Myddfai Steep Belt after Woodcock (1984a); Monian Composite Terrane after Gibbons and Horák (1990). Key: ADF, Aber-Dinlle Fault; BSZ, Berw Shear Zone; CASZ, Central Anglesey Shear Zone; DNF, Dinorwic Fault; LTFZ, Llyn Traffwll Fault Zone; ?NECBF, postulated NE Charnwood Boundary Fault. The boundary of the Midlands Microcraton basement domain is outlined by the NECBF and Pontesford-Myddfai lineament systems; WBFS, Welsh Borderland Fault System.

3

Figure 3.1: Figure 1.1 by Pharaoh& Carney (2000, p.3). Displays the Precambrian bedrock of England and Wales.

Table 3.2: The volume of 2.5M HCL to elute Sr during ion chromatography, calculated by Prof. Jane Evans depending on the calibration of the Dowex AG 50W-X8 resin.

From (date)	To elute waste solution (mL)	To elute Sr (mL)
02/06/14 - 12/04/15	46	12
13/04/15 - 25/10/16	54	12
26/10/16 - present	40	12

Table 3.3: The $^{87}Sr/^{86}Sr$ and Sr ppm results for the NIST Standard Reference Material 1515 (Apple Leaves), along with calculated average and 2SD. NIST 1515 Sample Number 4 was unsuccessful during TIMS.

NIST 1515 Sample Number	$^{87}Sr/^{86}Sr$	Sr ppm
1	0.713948	23.5
2	0.713971	23.3
3	0.713959	24.2
5	0.713937	26.2
6	0.713952	26.1
7	0.713937	22.2
8	0.713969	27
9	0.713944	25
10	0.71394	24.6
11	0.713958	26.1
12	0.713945	26.6
13	0.713895	27.4
14	0.713988	24.6
15	0.71392	26
Mean	0.713947	25.2
2SD	0.000045	3.1
%2SD	0.006	12.2

4. The Sr-isotope biospheres in England and Wales

4.1. The Sr-isotope biosphere of Charnwood Forest: a preliminary study

Charnwood Forest is located in Leicestershire in England (Figure 1.3 in chapter 1) and is the most centralised location of Precambrian bedrock within England. The rugged topography of this area is defined by its contrast between the bedrock lithologies of the older Precambrian, Cambrian and Ordovician to the earlier Triassic (Carney, 1999; LRWT, 2009). This bedrock geology is described further in section 4.1.1 below. It is not just the occurrence of Precambrian bedrock that makes Charnwood Forest interesting, it also has 21 sites of Special Scientific Interest which include a variety of woodlands, grasslands and wetlands (LRWT, 2009) as well as a rich heritage of prehistoric archaeology, with the Neolithic stone axe industry and prehistoric pottery being well renowned and sourced to the relatively small rock outcrops found within Charnwood Forest (Bradley, 1989a,b; Knight, 2002; Knight *et al.*, 2003; Loveday, 2004; McGrath, 2006; Williams, 1992).

The nearest biosphere $^{87}Sr/^{86}Sr$ values available to Charnwood Forest come from a plant sample with a $^{87}Sr/^{86}Sr$ = 0.71283 (JMPD_19), taken from the Triassic Sherwood Sandstone Group (NIGL, unpublished results) and a mineral water analysed by Montgomery *et al.* (2006) with $^{87}Sr/^{86}Sr$ = 0.709631 (JMW35), taken from the Triassic Mercia Mudstone Group. The $^{87}Sr/^{86}Sr$ from the mineral water sample (JMW35) is in line with the other mineral water samples taken from Triassic sandstones in Montgomery *et al.* (2006) and with the other biosphere $^{87}Sr/^{86}Sr$ = 0.7097 ±0.0006 (n=25, 1σ) based on Triassic bedrock in Evans *et al.* (2010). However, the plant sample (JMPD_19) is more radiogenic than seen in other biosphere proxy samples currently on Triassic bedrock.

Other than above, no other biosphere data is available within a 20km radius of Charnwood Forest. This, along with the Precambrian bedrock, made the area a good starting point for a preliminary study.

4.1.1. Geological Summary of Charnwood Forest

The lithologies present in Charnwood Forest extend from the Precambrian through to the Triassic, with the earliest deposition being the Quaternary superficial deposits. The rocks from the Precambrian form inliers (older rock formations surrounded by younger rocks) and together are part of the Charnwood terrane: a terrane is a large proportion of crustal geology that is exotic with respect to the geology either side of it. The Charnwood terrane also includes the Precambrian inlier near Nuneaton (discussed in section 4.3) (Pharaoh *et al.,*1987*a*). The Precambrian bedrock in Charnwood Forest can be split into the Charnian Supergroup and the Charnwood diorites. Overlying these is the Brand Group, which dates to the Cambrian and lying in between these older lithologies is the much younger Triassic Mercia Mudstone Group. Finally overlying all these bedrocks are Quaternary superficial deposits (Carney, 1999, 2010; Carney *et al*., 2000; LRWT, 2009). Immediately adjacent to all of the above bedrocks is the Ordovician Mountsorrel Igneous Complex, which is often included within an extended Charnwood *sensu lato* (LRWT, 2009; Pharaoh *et al.,* 1993). A geological map of the Precambrian basement rocks of Charnwood Forest by Carney (1999) can be viewed in Figure 4.1.1, while all the bedrock geology can be seen in Figure 4.1.2, along with plant $^{87}Sr/^{86}Sr$ data from the Charnwood Forest study area.

4.1.1.1. The Charnian Supergroup and the Charnwood Diorites (Precambrian)

Of all the different ages of rocks present in Charnwood Forest it is the Precambrian rocks of the Charnwood terrane that have gained the most interest (with publications on these rock formations dating back to 1790; Carney, 1999). Within this terrane is the Charnian Supergroup, a ~3.5km thick volcaniclastic succession that forms an anticline, and the Charnwood diorites (described further below). The Charnian Supergroup can be split into two groups, the Blackbrook Group and the Maplewell Group which both date to the Neoproterozoic Era of the Precambrian (approximately 615-560Ma; Carney, 2010; Compston *et al.*, 2002; LRWT, 2009). The Blackbrook Group consists of well bedded to laminated volcaniclastic mud-, silt- and sandstones, with some volcaniclastic breccia. The Maplewell Group consists of volcaniclastic and tuffaceous (where pyroclastic grains form 25-75% of the rock) mud-, silt- and sandstones with glass-like (vitric) tuffs and volcanic block-breccias (mainly dacitic). The Maplewell Group contains the greatest volume of pyroclastic material and so these rocks are believed to have formed during the time of maximum volcanic activity (Carney, 2000; Carney, 2010). The majority of the rocks in these groups are sedimentary but have volcanic inputs. The only parts of the Charnian Supergroup that are primarily of magmatic origin are the Bardon Hill and Whitwick complexes within the Maplewell Group (see Figure 4.1: Pharaoh *et al.,* 1987*b*). It is believed that the Neolithic stone axes famous in this area, were most likely sourced from the Precambrian outcrops of the Whitwick complex, around the Blackbrook reservoir (Bradley 1989a; 1989b).

The plate-tectonic and depositional environment of the Charnian Supergroup has been described as being in moderately deep water nearby to a calc-alkaline volcanic arc (Carney *et al.,* 2000). A modern day analogy for this setting can be seen on the island of Montserrat (Ambrose *et al.,* 2007) or better still Japan (Le Bas, 1982). Calc-alkaline volcanism can produce a variety of different igneous rocks, from mafic basalts through to felsic rhyolites and their coarser grained intrusive equivalents, gabbro and granite respectively. So within the sedimentary rocks of the Blackbrook and Maplewell Groups can be volcanic inputs that range from mafic to felsic compositions. The Bardon and Whitwick complexes have magmatic origins and consist mainly of porphyritic dacite and andesite or dacite breccia (BGS lexicon; Carney, 2010; Pharaoh *et al.,* 1987*b*).

Prior to the end of the magmatic activity during the Precambrian, the Charnian Supergroup was intruded by a series of diorites (intermediate in composition) known as the North and South Charnwood Diorites (Figure 4.1). They are believed to represent either a late Neoprotozoic event or a very early Cambrian event (Carney, 2010; Cribb, 1975; Le Bas, 1982). Cribb (1975) studied the Rb-Sr and $^{87}Sr/^{86}Sr$ of igneous rocks present in Leicestershire. This included the North and South Charnwood Diorites, with the North Diorites recorded whole-rock $^{87}Sr/^{86}Sr$ =0.70808-0.70880, while the South recorded values between 0.71193 - 0.71535 (both ranges had varying discrepancies).

4.1.1.2. The Brand Group (Cambrian)

The Brand Group overlies the Maplewell Group and once was considered part of the Charnian Supergroup. It was reassessed with the discovery of the Cambrian trace fossil

Teichichnus by B. Bland in 1992 and now the majority of this group is considered to be part of the lower Cambrian (~543Ma, the earliest part of the Paleozoic Era: Carney, 2010; McIlroy, *et al*., 1998). The age and stratigraphical assignation of the Hanging Rocks Formation, consisting mainly of conglomerates and volcaniclastic sandstones, within the Brand Group still remain uncertain (Carney, 2010). However, the Brand Hill and Swithland Formations that follow are both firmly considered Cambrian in age. The Brand Hill Formation consists mainly of quartz-arenites and wackes (types of sandstone) interbedded with mudstones, while the Swithland Formation contains slaty mudstones and greywackes, with thin conglomeratic sandstones (Carney, 2010; McIlroy *et al*., 1998).

4.1.1.3. The Mountsorrel Igneous Complex (Ordovician)

During the Caledonian orogeny, dating from the Ordovician to early Devonian (Carney *et al.,* 2008), the Mountsorrel Igneous Complex intruded into the Cambrian to Ordovician slaty mudstones of the adjacent Mountsorrel area, on the eastern flank of Charnwood Forest (see Figure 4.2). The outcrops of the Mountsorrel Igneous Complex are quite small, covering approximately $4km^2$ and are often referred to as an extension of the Charnwood Forest area. The complex mainly consists of granodiorite, but also contains diorite and gabbro. These rocks have been dated to the late Ordovician (~440-446Ma) and were formed within a calc-alkaline magmatic arc setting when England was part of a small continent called Avalonia (Carney *et al.,* 2008; Pharaoh *et al.,* 1993). The whole-rock $^{87}Sr/^{86}Sr$ of the granodiorites from this complex were recorded in Cribb (1975), with values ranging from 0.70957 - 0.71644 (with varying discrepancies). The outcrops of the Mountsorrel Igneous Complex are also the source of distinctive granitic inclusions found within prehistoric pottery from the Iron Age found in the Midlands (Knight, 2002, p138-140; Knight *et al.*, 2003; Williams, 1992), as well as Charnwood ware from the early to middle Saxon period (Williams & Vince, 1997).

4.1.1.4. The Mercia Mudstone Group (Triassic)

During the Triassic period, the older Precambrian to Cambrian rocks of Charnwood Forest were passively buried by 'red beds' of the Mercia Mudstone Group. These 'red beds' were deposited in the Hinckley Basin and are dominated by massive red-brown mudstones and subordinate siltstones, with some thick halite-bearing units in basinal areas. The majority of these 'red beds' are thought to be deposited through wind action in subaqeuous playas or inland sabkha environments (Warrington *et al.*, 1980; Carney, 2010).

4.1.1.5. Quaternary Superficial Deposits

The current topography of Charnwood Forest has been sculptured by repeated glaciations in the Quaternary. The hard Precambrian, Cambrian and Paleozoic rocks of the area provided a source of large glacial erratics which can be found to the south of the Charnwood area. For example the Humberstone, which is found on the eastern outskirts of the city of Leicester, can be convincingly shown to be granodiorite from the Mountsorrel Igneous Complex. Glacial till deposits, as well as glacial sand and gravels are mainly found upon the Triassic Mercia Mudstone Group. The ice sheets of the more recent glaciations in the Quaternary did not reach far enough south to directly affect Charnwood Forest, but were indirectly responsible for widespread periglacial head deposits in the surrounding area (LRWT, 2009; BGS, 2010, Sheet 155).

4.1.2. Geochemical Survey and Field-notes for Charnwood Forest

In March 2014 a total of nine locations were visited in Charnwood Forest study area. Each analytical sample in this study consisted of single plant, for example if oak leaves were collected they all came from the same tree. At some of the locations, up to three single plants were collected, resulting in three analytical samples. One sample was collected from a tree, another from a shrub and the last from a low-lying plant, such as a grass, bracken or herb. These samples were collected with the intention of comparing their $^{87}Sr/^{86}Sr$, to see if there is any difference in value depending on the plant type chosen.

The weather over the collection period was sunny with cloudy spells and the wind was calm. All the plant samples collected were sealed in separate kraft sample bags or brown paper envelopes labelled with sample code, date and name of plant if known, and allowed to dry naturally. Field-notes of the plant samples collected from across

Charnwood Forest can be viewed in the Appendix 2. The Charnwood Forest plant samples followed the same methods for chemical preparation and Sr-isotope analysis outlined in section 3.3 in Chapter 3.

4.1.3. Plant $^{87}Sr/^{86}Sr$ Results

The $^{87}Sr/^{86}Sr$ of the plant samples from across Charnwood Forest can be seen in Figure 4.1.2 and Figure 4.1.3. Altogether the plant $^{87}Sr/^{86}Sr$ = 0.7109 ±0.0011 (n= 16, 2SD). If split, based on the bedrock geology, the Precambrian Charnian Supergroup has a plant $^{87}Sr/^{86}Sr$ = 0.7107 ±0.0005 (n=10, 2SD), while the Precambrian Charnwood Diorites have plant $^{87}Sr/^{86}Sr$ of 0.71058 (CHW 07) and 0.71040 (CHW 08), the Ordovician Mountsorrel Igneous Complex has a plant $^{87}Sr/^{86}Sr$ of 0.71098 (CHW 01) and the Triassic Mercia Mudstone Group has a plant $^{87}Sr/^{86}Sr$ = 0.7119 ±0.0008 (n=3, 2SD).

The plant $^{87}Sr/^{86}Sr$ values from the Precambrian Charnwood Diorites and the Ordovician Mountsorrel Igneous Complex both fall within 2SD of the plant $^{87}Sr/^{86}Sr$ of the Precambrian Charnian Supergroup, making them hard to distinguish from one another in the Sr-isotope biosphere. The Precambrian Charnian Supergroup and Charnwood Diorites can be considered as one distinctive biosphere, with a plant $^{87}Sr/^{86}Sr$ = 0.7107 ±0.0005 (n=12, 2SD), but for now as the Mountsorrel Igneous Complex is Ordovician in age it should remain separate. The plant $^{87}Sr/^{86}Sr$ from the Triassic Merica Mudstone Group are more distinct from the Precambrian lithologies (Figure 4.2 and 4.3), having an average difference of approximately +0.001. Altogether none of the plant $^{87}Sr/^{86}Sr$ in Charnwood Forest have produced radiogenic values >0.714.

There is no significant difference (approximately +0.001 or greater: chapter 2, section 2.2) between the $^{87}Sr/^{86}Sr$ of different plant types, e.g. a tree, shrub or low-lying plant (like grass), on the same bedrock geology in the Charnwood Forest study area (Figure 4.4). The variations between the different plant types vary between +0.0002 to +0.0007 depending on the location. At the 4th significant figure, these differences can be seen as irrelevant and an expected form of natural variation in the $^{87}Sr/^{86}Sr$ value (see chapter 2, section 2.2).

The plant samples CHW 05, CHW 10 and CHW 12 were unsuccessful in their first and second repeated runs for Sr isotope analysis by TIMS at the NIGL (Keyworth). New plants samples for these locations were not re-collected as it was deemed unnecessary considering the $^{87}Sr/^{86}Sr$ values already recorded from the other successful plant samples from Charnwood Forest.

4.1.4. Discussion of plant $^{87}Sr/^{86}Sr$ from Charnwood Forest

Although the bedrock geology in Charnwood Forest has Precambrian rocks with volcanic origins and the Ordovician Mountsorrel Igneous Complex *sensu lato*, none of the plant $^{87}Sr/^{86}Sr$ have values >0.714. The calc-alkaline volcanism that occurred in the Precambrian can form rocks that range from mafic to felsic in composition, however the majority of the Precambrian rocks in Charnwood Forest are sedimentary, just with volcanic inputs (section 4.1.1). The felsic rocks, which would have most likely provided the radiogenic$^{87}Sr/^{86}Sr$, are clearly not dominant in any of the Precambrian lithologies in Charnwood Forest. Even the plant sample CHW 06 which was believed to be rooted in an exposure of rhyolite (felsic in composition) had a $^{87}Sr/^{86}Sr$ = 0.71110, which was less radiogenic than expected. This plant sample, along with plant sample CHW 13 with a $^{87}Sr/^{86}Sr$ at 0.71118, are the most radiogenic values based on the Charnian Supergroup. Both were directly rooted in rock exposures (Appendix 2). It is possible that rock rooted plants have access to more radiogenic Sr from the mineral decomposition of the rock they are rooted in and therefore are expected to have the highest $^{87}Sr/^{86}Sr$ from such bedrock. However, such values are also produced by unusual circumstances, as most plant samples collected are not directly rooted in exposed rock. If they are excluded from the Precambrian average, the plant $^{87}Sr/^{86}Sr$ becomes 0.7106 ±0.0002 (n=8, 2SD), resulting in a difference of -0.0003 in the 2SD.

The average Precambrian plant $^{87}Sr/^{86}Sr$ above from Charnwood Forest study area compares best with the Proterozoic, Dalradian with $^{87}Sr/^{86}Sr$ = 0.7097 ±0.0003 (n=4, 1SD) reported by Evans *et al.* (2010). Other Precambrian sedimentary lithologies have produced biosphere $^{87}Sr/^{86}Sr$ ranging from approximately 0.7110 to 0.7165 (Evans *et al.*, 2010). Overall the Precambrian plant $^{87}Sr/^{86}Sr$ from Charnwood Forest falls towards the lower values expected from such lithologies.

The granodiorites of Mountsorrel Igneous Complex have whole rock $^{87}Sr/^{86}Sr$ ranging from 0.70957-0.71644 (±0.00005: Cribb, 1975), however the plant $^{87}Sr/^{86}Sr$ =

0.71098 (CHW 01). This plant sample was directly rooted into exposed rock (Appendix 2), so as observed above, its $^{87}Sr/^{86}Sr$ value is expected to reflect the most radiogenic Sr currently bioavailable to the plant from this bedrock. It is unlikely that radiogenic $^{87}Sr/^{86}Sr$ >0.714 will be produced from the biosphere on the Mountsorrel Igneous Complex considering its size (~4km^2) and intermediate to mafic composition.

The plant $^{87}Sr/^{86}Sr$ = 0.7119 ±0.0008 (n=3, 2SD) on the Triassic Mercia Mudstone Group and are the most radiogenic values seen in Charnwood Forest currently (Figure 4.1.3 and 4.1.4). When compared to the biosphere $^{87}Sr/^{86}Sr$ = 0.7097 ±0.0006 (n=25, 1SD) on Triassic bedrock in Evans *et al.* (2010), the plant $^{87}Sr/^{86}Sr$ from Charnwood Forest are more radiogenic by approximately +0.0022. There was no concern raised during the geochemical survey (Appendix 2) or from the chemical procedure and Sr-isotope analysis. The plant sample (JMPD_19) on the Triassic Sherwood Sandstone Group, with a $^{87}Sr/^{86}Sr$ of 0.71283 (NIGL, unpublished results), is also more radiogenic than seen in Evans *et al.* (2010). Interestingly, the biosphere proxy types used in Evans *et al.* (2010) to produced the average Triassic $^{87}Sr/^{86}Sr$ only included water, soil and bone/dentine samples. It could be that plants based on Triassic bedrock are able to access more radiogenic Sr than recorded by other biosphere proxy types. Collection of further plant samples based on Triassic bedrock would be useful to see if this trend continues.

4.1.5. Concluding remarks

Overall none of the plant samples from across Charnwood Forest have $^{87}Sr/^{86}Sr$ values >0.714. The Sr-isotope biosphere for Charnwood Forest at present, is as follows:

- The Precambrian Charnian Supergroup plant $^{87}Sr/^{86}Sr$: 0.7106 ±0.0002 (n=8, 2SD), and two elevated plant $^{87}Sr/^{86}Sr$ at 0.71111 and 0.71118 (CHW 13), both of which were rooted in exposed Precambrian bedrock.
- The Precambrian Charnwood Diorites plant $^{87}Sr/^{86}Sr$: 0.71058 (CHW 07) and 0.71040 (CHW 08).
- The Ordovician Mountsorrel Igneous Complex plant $^{87}Sr/^{86}Sr$: 0.71098 (CHW 01), this sample was also rooted in exposed bedrock.
- The Triassic Mercia Mudstone Group plant $^{87}Sr/^{86}Sr$: 0.7119 ±0.0008 (n=3, 2SD).

4.1. Figures

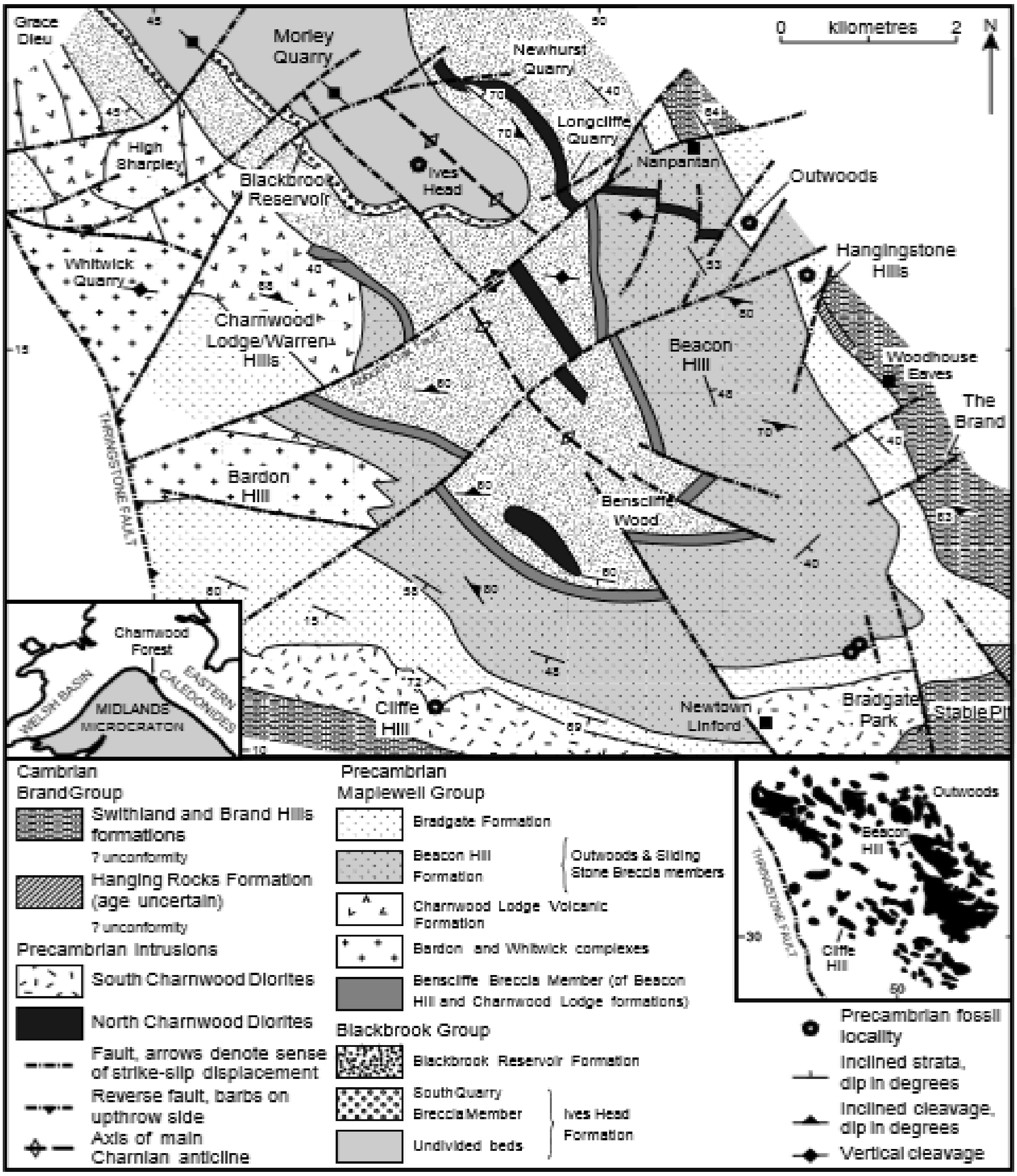


Figure 4.1.1 Figure 2 taken from Carney (1999, p.222). A geological map showing the distribution of the Precambrian basement rocks of Charnwood Forest and the numerous inliers (dark areas of inset at lower right) which protrude through the Triassic Mercia Mudstone Group.

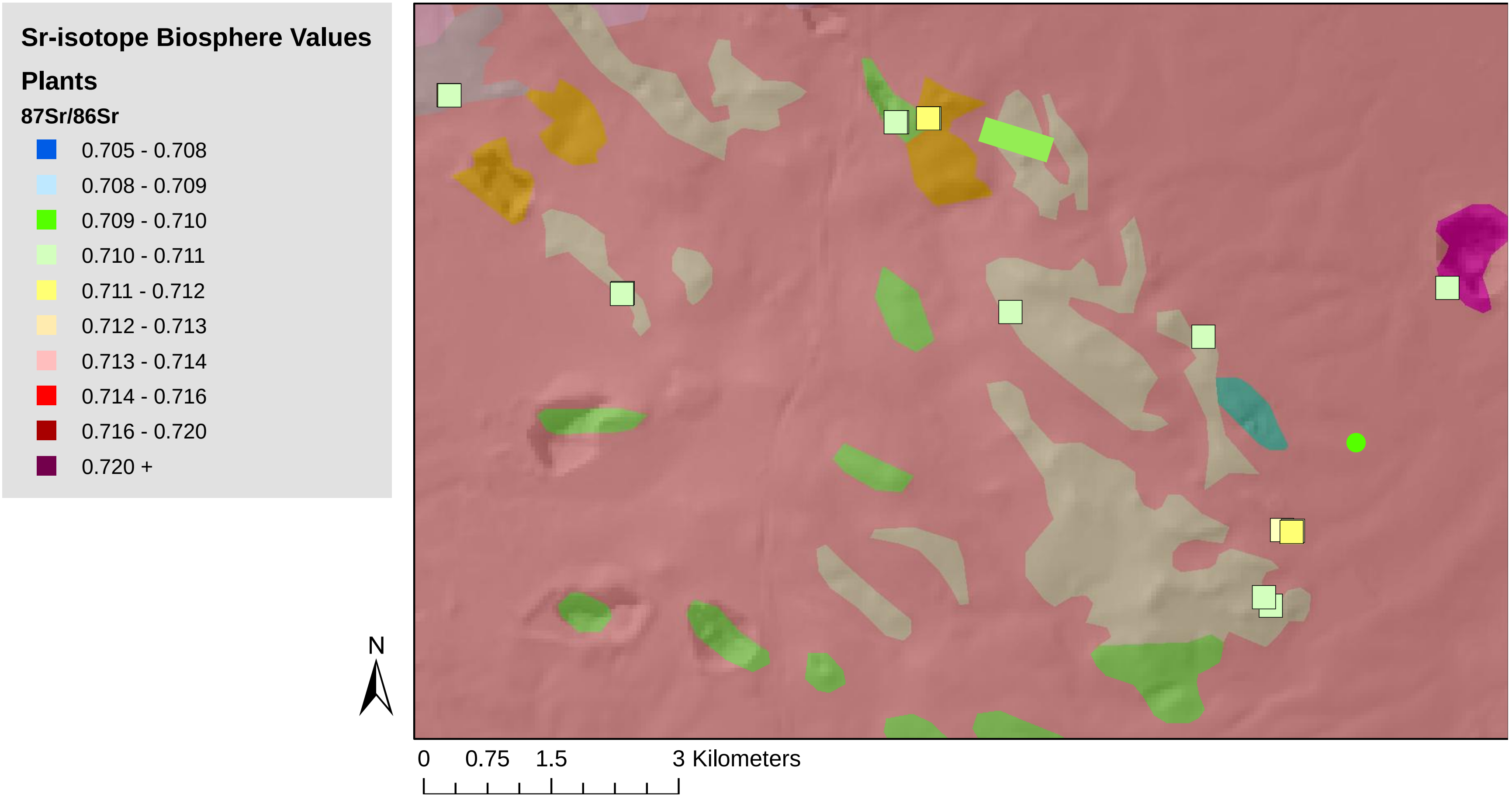


Figure 4.1.2. The plant $^{87}Sr/^{86}Sr$ (outlined squares) from across the Charnwood Forest study area, alongside GIS data of the 1:625000 Bedrock maps (BGS, DiGMapGB, 2007). The main legend for the Bedrock geology can be seen in Figure X. The water sample (circle, not outlined) is JMW 35 (Montgomery *et al.*,2006) and it has the same colour and value scheme as seen in the legend of the plant$^{87}Sr/^{86}Sr$. .

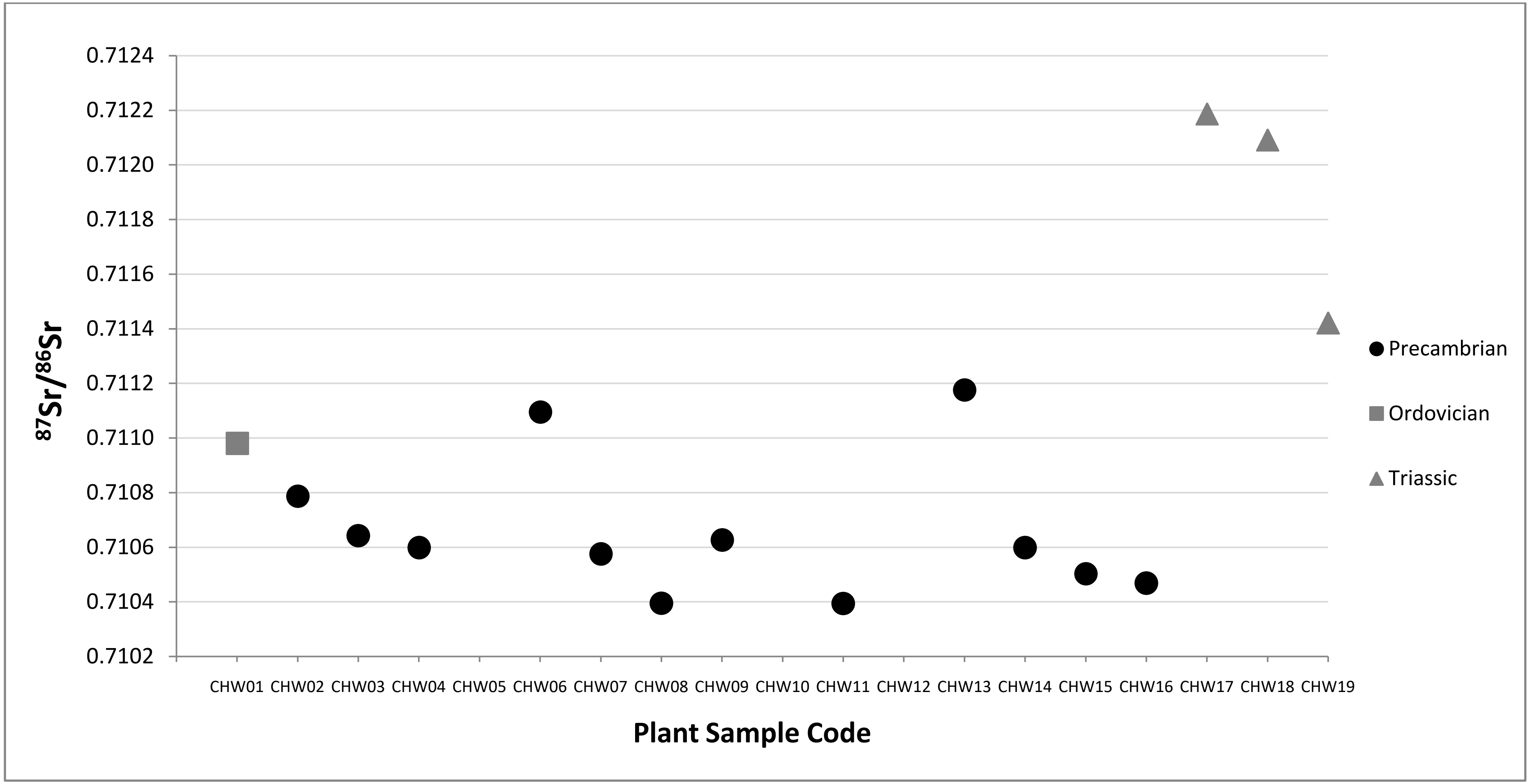


Figure 4.1.3._The plant $^{87}Sr/^{86}Sr$ results from across Charnwood Forest based on age of the bedrock geology. The plant samples CHW05, CHW10 and CHW12 were unsuccessful (see section 4.1.3).

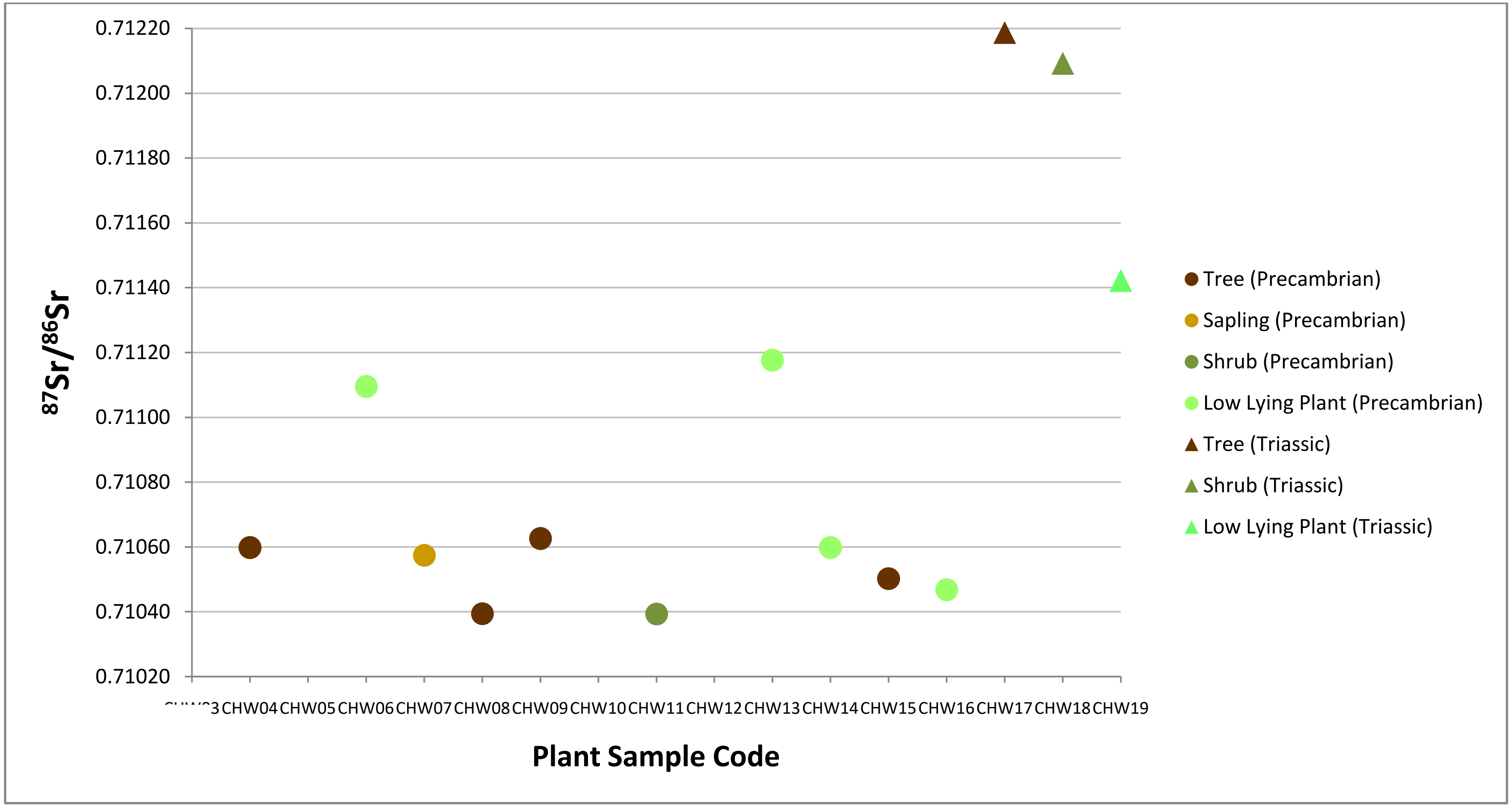


Figure 4.1.4. The plant $^{87}Sr/^{86}Sr$ results for Charnwood Forest based on plant type (e.g. tree, shrub or low lying plant) and age of bedrock geology. The plant samples CHW 01, CHW 02 and CHW 03 are not included as only one plant type was taken at each locati**on**.

4.2. The Sr biosphere of the Malvern Hills: a preliminary study of mixed plant samples.

The Malvern Hills (Figure 1.3 in chapter 1) stretch across the English counties of Worcestershire, Herefordshire and northern Gloucestershire. Consisting of several peaks, these hills extend approximately 13km from the southern Chase End Hill to the, appropriately named, North Hill; the highest summit is the Worcestershire Beacon at approximately 425m above sea level. They are known for their outstanding natural beauty and spring water, in which the spa-town Great Malvern developed in the 19th century (a sample of this spring mineral water has been analysed by Montgomery *et al.,* 2006).

The Malvern Hills are made up of a suite of plutonic igneous and metamorphic rocks,which date to the late Precambrian (in the Neoproterozoic era ~670Ma: Beckinsale *et al.,* 1981: Thorpe *et al.,* 1984: Tucker & Pharaoh, 1991). They are referred to as the Malvernian Igneous Complex, or more briefly as the Malvern Complex. This complex is exposed by a series of east-west faults termed the Malvern Lineament (PIC). Younger sedimentary formations the Cambrian to Silurian lie to the west and the Triassic to the east. The Malvern Lineament splits the Malvern Complex into seven blocks, with the least altered igneous rocks in the most northern block and progressive deformation increasing towards the southern block (Figure 4.2.1: Lambert & Holland, 1971).

Plant $^{87}Sr/^{86}Sr$ >0.714have been recorded from the Malvern Hills by Chenery *et al.* (2010)and Evans (unpublished results; *pers.com*.). The highest $^{87}Sr/^{86}Sr$ value at 0.71622 was recorded directly above the Precambrian volcanic bedrock near to Hollybush (Ledbury: Chenery *et al.,* 2010). However, altogether the plant $^{87}Sr/^{86}Sr$ from across the Malvern Hills can range from 0.709 - 0.716 (Chenery *et al.,* 2010; Evans, unpublished results*; pers.com*.), reflecting the varying bedrock geology of the Malvern Hills and surrounding area (approximately 20km^2). There is also the mineral water (JMW 07) with a $^{87}Sr/^{86}Sr$ = 0.713288 taken on the Precambrian Malvern Complex (Montgomery *et al.,* 2006), as well as water samples based on the Triassic lithologies to the east from Spiro *et al.* (2001), with$^{87}Sr/^{86}Sr$ = 0.7099 ±0.0014 (n=13,2SD).

The Malvern Hills study area is the first site in which several plants over a given area were collected with the intention of mixing them to create one analytical sample seen in section 3.2.2 and 3.2.3 in chapter 3. Further information about this can be found in section 4.2.3 below. The main aim for this study area is to find out if $^{87}Sr/^{86}Sr$ values >0.714 are reproducible in the Malvern Hill's biosphere.

4.2.1. Geological Summary of the Malvern Hills

The first geological paper on the Malvern Hills was given by Leonard Horner in 1810 to the Geological Society (which had only been founded in 1807) titled *'On the mineralogy of the Malvern Hills'* (Raw, 1951).This paper first identified 'granitic' rocks of the Malvern Hills, compared to the sedimentary rocks on either side. Since then many of the geological studies relating to the Malvern Hills have been biased towards the Precambrian Malvern Complex. Its Precambrian age was first expressed by Holl in 1865 and has since been confirmed by isotope analysis. Overall, the isotope data indicates an intrusion age of around ~670Ma for the complex (U-Pb zircon age at 677 ±2Ma; U-Pb monazite age at 670 ±10Ma; Rb-Sr whole-rock age at 681 ±53Ma: Beckinsale *et al.,* 1981: Thorpe *et al.,* 1984: Tucker & Pharaoh, 1991: in Pharaoh & Gibbons, 1994, p.90). When compared to the isotopic data from other igneous Precambrian suites within England, the Malvern Complex displays the oldest markers for intrusive igneous activity (Tucker & Pharaoh, 1991). This has made the complex a unique area of geological interest in England.

The bedrock geology of the Malvern Hills area and, even the internal lithology of the Malvern Complex itself, is complicated. Consequently, the geological summary has been split under titles of geological age rather than the important formations. At present, the most detailed geological map publically available is at a scale of 1:50,000 by the BGS (1988, Solid & Drift, Sheet 216; 1993, Solid & Drift, Sheet 199). Lambert & Holland (1971, p.327) state that to map the Malvern Complex would *'require a scale of 1:2500 or even larger, so rapid is the variation of rock types'*. Therefore, the bedrock geology described further below has been summarised and is specific to the area needed for this study, e.g. a transect between Tewkesbury and Ledbury. A simplified geological map of the Malvern Hills, showing mainly the blocks of the Precambrian Malvern Complex, can be viewed in Figure 4.2.1. All of the bedrock geology for the Malvern Hills study area is displayed in Figure 4.2.2, along with the locations of plant samples.

4.2.1.1 Precambrian (Neoproterozoic)

The Precambrian Malvern Complex consists of a varied assemblage of plutonic igneous and metamorphic rocks, with diorites, tonalites and granites together forming 95% of the complex (Lambert & Holland, 1971). The remaining rocks are either plutonic ultramafic rocks or the metamorphosed, or hybridized, equivalents of the above plutonic rocks. The majority of the Malvern Complex has been affected by hydrothermal alterations and strong, dynamic deformation through its long geological history, this deformation intensifies southwards along the hills (Dunning, 1975; Lambert and Holland, 1971; Beckinsale *et al*., 1981; Worssam *et al.,* 1989; Pharaoh & Gibbons, 1994, p.90). The complex is also cut by several igneous intrusions (such as dykes); most are microdiorites or dolerites (Lambert & Holland, 1971) and there is one example of an unusual late, potash-rich trachyte which was recorded by Thorpe (1972) at Earnslaw Quarry. For this study, only the 4th, 5th and 6th blocks of the Malvern Complex were sampled from (the southern blocks in Figure 4.2.1).

In more specific geological detail, the 4th block, which contains Swinyard Hill can be split in two. The northern half contains massive granites foliated granites, sheared granites, sheared diorites, biotite-schists (containing high proportions of the mineral garnet) and the diorite and epidiorite complex of the Gullet Quarry. The southern half has similar rocks to above, but with what Lambert & Holland (1971, p.330) describe as mappable metamorphic structures, as well as chlorite-schists and pegmatites. The 5th block, with Midsummer Hill, consists of sheared, hydrolysed diorites and chlorite-schists, cut by pegmatites and occasional dykes. The 6th block, which contains Raggedstone Hill, mainly consists of chlorite-schists (theses are thought to have once been diorites) with some pegmatites (Lambert & Holland, 1971, p.330). Finally, the majority of the southern half of the complex is overlain unconformably by the Malvern quartzite of the Lower Cambrian, which shows a lot less deformation and metamorphism compared to the Precambrian lithologies above(Pharaoh& Gibbon, 1994, p.90).

The Warren House Group or Volcanic also dates to the Neoproterozoic in the Precambrian, occupying a small area (~1km^2) on the eastern flank of the Malvern Hills (Figure 4.2.1). This group consist of mainly volcanically erupted altered basalts (possibly exhibiting pillow-lava structure) and are associated with minor amounts of 'keratophyres' (altered intermediate rocks), rhyolites and crystal-vitric tuff (possibly being ignimbrite: Lambert & Holland, 1971; Pharaoh *et al.,* 1987b; Worssam *et al.,* 1989). The Warren House Group is in presumed fault contact with the Malvern Complex (Worssam *et al*., 1989) and has yielded an eruption age of 566±2Ma through the isotopic analyses (U-Pb zircon ages) of some of its rhyolithic tuffs (Tucker & Pharaoh, 1991). Although not directly sampled from, the Warren House Group is worth considering as the erosion and weathering products of these Precambrian rocks may contribute to the Sr-isotope biosphere in the 4^{th} block of the Malvern Complex (Figure 4.2.1).

The chemical variations of the Precambrian rocks in the Malvern Complex are described as having a calc-alkaline affinity (with low Nb content: Lambert & Holland, 1971; Thorpe 1972; Thorpe *et al.* 1984; Tucker & Pharaoh, 1991). This is characteristic of volcanic arc magmatic suites (Thorpe, 1972: Thorpe *et al.,* 1984) and produces a similar situation as described previously in section 4.1.1 in the Charnwood Forest study. This is where the composition of the rocks varies from mafic through to felsic within the same complex and so can lead to varying inputs of $^{87}Sr/^{86}Sr$ from the bedrock geology.

4.2.1.2. Cambro-Ordovician

Lying unconformably and to the west of the southern half of the Malvern Complex are the Cambrian lithologies. These Cambrian lithologies can be subdivided into the Malvern Quartzite. These are hard quartz-cemented sandstones interbedded with conglomerates (often containing clasts and debris from the Precambrian Malvern Complex), the Hollybush Sandstone, a ~300m thick succession of mainly green micaceous sandstones (mica mainly derived from the Precambrian Malvern Complex) with thin conglomerates and impure limestones, and the White-Leaved Oak Shale, dark grey to black metamorphised mudstones. Faulting has brought these Cambrian lithologies in contact with the Ordovician Bronsil Shale, which consists of silver-grey metamorphised mudstones. There are also a number of igneous intrusions that occur throughout the Cambrian succession above, mainly mafic dykes and sills, which are of presumed Ordovician age (Worssam *et al.*, 1989). The Cambrian lithologies are grouped into the Ordovician (Tremadocian) mud-, silt- and sandstones in Figure 4.2.2, but can be seen in the 1:50,000, Sheet 216 map by the BGS, (1988, Solid and Drift Geology).

4.2.1.3. Siluro-Devonian

Only the Siluro-Devonian lithologies from the southern Malvern Hills are described below, but there are a wide range of successions and formations that date between the Silurian and Devonian, with Silurian lithologies dominating, in the Tewkesbury district (BGS, 1988, Sheet 216). The Silurian lithologies lie unconformably with both the Cambro-Ordovician bedrock and the Precambrian Malvern Complex described above. In descending age westwards from the Malvern Complex, the Silurian successive formations include: the May Hill Sandstone (Llandovery); Woolhope Limestone (Wenlock); Wenlock Shale (Wenlock); Wenlock Limestone (Wenlock); Lower Ludlow Shale (Ludlow); Aymestry Limestone (Ludlow); Upper Ludlow Shale (Ludlow); Downton Castle Sandstone (Pridoli); the Siluro-Devionian Raglan Mudstone (Pridoli to Devonian), which is part of the Old Red Sandstone (ORS) assemblage. Many of the mudstone lithologies can be described as calcareous, but some are also micaceous (mainly within the May Hill Sandstone and Raglan Mudstone).The older Siluiran May Hill Sandstone formation can also contain conglomerates which include clasts derived from the Precambrian Malvern Complex (Worssam *et al.,* 1989).

4.2.1.4. Permian-Triassic

During the Permian and Triassic, Britain was near the middle of the massive 'super-continent' of Pangaea, at low northern latitudes that resulted in hot desert climate. The Permian-Triassic bedrock lies to the south and east of the Malvern Hills and was deposited in the Worcester Basin. The Permian formations of interest in this study include: the Haffield Breccia, which contains clasts derived from both Precambrian Malvern Complex and Silurian May Hill Sandstone; the Bridgnorth Sandstone, mainly red to brown, well sorted, medium to coarse grained sandstones. The Triassic bedrock includes: the Bromsgrove Sandstone of the Sherwood Sandstone Group, which are mainly conglomerates, sandstones and mudstones; the Mercia Mudstone Group, a succession of massive red-brown silty mudstone. In the Malvern Hills study area, the Mercia Mudstone Group is commonly scattered with green-grey spots and patches, often containing small nodules of anhydrite and gypsum (Worssam *et al.,* 1989).

4.2.1.5. Quaternary Superficial Deposits

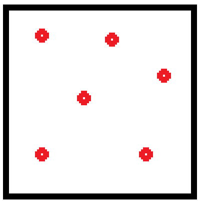
The Malvern Hills has experienced repeated glaciations during the Quaternary period. The last time ice sheets covered the Malvern Hills was during the Middle Pleistocene Anglian Ice Stage (approximately 0.3 million years ago: Worssam *et al*., 1989). Other younger glaciations either just penetrated or halted before the north of Worcestershire and therefore failed to reach the Malvern Hills. From the Middle Pleistocene to the start of the Holocene, the whole Malvern Hill area has been subjected to repeatedly periglacial processes, with permafrost and a tundra climate being common conditions (Worssam *et al*., 1989). The main Quaternary superficial deposits near the Malvern Hills are river terraces and head deposits, which contain material of the local rock lithologies. Larger superficial deposits mainly occur across the Triassic Mercia Mudstone Group to the east and in valley bottoms of the Siluro-Devonian Raglan Mudstone (part of the ORS) to the west (BGS, 1988, Sheet 216; Worssam *et al*., 1989; Chernery *et al.*, 2010). The other bedrocks within the Malvern Hills are only partially covered according to the BGS, 1:50000 map (1988, Solid and Drift Geology, Sheet 216).

4.2.2. Geochemical Survey and Field-notes for the Malvern Hills

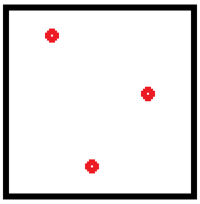
Mixed plant samples were collected for the first time in this study (chapter 3, section 3.2.2 and 3.2.3). Three plants were collected from three different locations within 1km^2 to make one analytical sample. This was repeated, collecting from the same locations, resulting in two mixed plant samples per 1km^2, labelled A and B. In total eleven 1km^2 'boxes' were collected from across the Malvern Hills study area (Figure 4.2.2), resulting in 22 mixed plant samples for Sr-isotope analysis.

The above method was chosen over the collection of six plants per 1km^2 (see depiction below). Collecting two mixed plant samples from the same 1km^2 'box' allows them to be compared and will distinguish if the mixing of plants is an appropriate geochemical survey method.

a



b



a: collect six plant samples from different locations, which will later be mixed to produce one anlytical sample per 1km^2.

b: collect from three different locations per 1km^2, collecting two plant samples from each labelledA and B. Mix the plants of set A together, and set B together, so two analytical samples, and therefore two^{87}Sr/^{86}Sr values are available per 1km^2.

In July 2014, a total of 33 locations were visited across the Malvern Hills. The weather over the collection period was sunny, with varying winds from a gentle breeze to brief gusts. Each 1km^2 had three locations within it and at each location two separate plant samples were collected, being apart by approximately 2 to 10m maximum. These were sealed in kraft paper sample bags and labelled with sample number and whether they were part of set A or B respectively. The date and the name of the plant, if known, were also noted on the sample bag and they were all allowed to dry naturally. Further field-notes on the plant samples and locations can be seen in Appendix 2.

All the plant samples in this study followed the same methods of chemical preparation and Sr-isotope analysis outlined in section 3.3 in chapter 3.

4.2.3. Plant ^{87}Sr/^{86}Sr Results

The ^{87}Sr/^{86}Sr results of the plant samples from across the Malvern Hills study area are displayed in Figure 4.2.3 and Table 4.2.1. None of the plant ^{87}Sr/^{86}Sr have recorded values >0.714, the highest being approximately 0.7135 taken from above the Precambrian Malvern Complex. The majority of the set A vs. set B plant ^{87}Sr/^{86}Sr from the same 1km^2 box show no significant difference between one another (e.g. +0.001 or greater), only showing change in the 4th significant figure. This can be seen as natural variation in the

$^{87}Sr/^{86}Sr$ value of plants (discussed in chapter 2, section 2.2) and is expected, considering the varying bedrock geology over Malvern Hills and even within the 1km^2 boxes themselves. However, exceptions can be seen in the 1km^2 box MB1, on Silurian sedimentary rock, and MB11, on the Triassic Mercia Mudstone Group. The difference between the plant $^{87}Sr/^{86}Sr$ of set A vs. set B in MB1 is +0.0015 and for MB11 is +0.0011. These two 1km^2 boxes are discussed further in section 4.4.4.1.

The plant $^{87}Sr/^{86}Sr$ for set A and set B are displayed alongside the bedrock geology in Figure 4.2.4. Altogether, the Precambrian Malvern Complex has a plant $^{87}Sr/^{86}Sr$ = 0.7133 ±0.0004 (n=4, 2SD), the sedimentary rocks of the Cambro-Ordovician have plant $^{87}Sr/^{86}Sr$ at 0.71203 (MB6 A) and 0.71286 (MB6 B), the Silurian sedimentary rocks have plant$^{87}Sr/^{86}Sr$ = 0.7105 ±0.0017 (n=10, 2SD) and the Triassic Mercia Mudstone Group have plant$^{87}Sr/^{86}Sr$ = 0.7114 ±0.0012 (n=6, 2SD).

4.2.4. Discussion of the plant $^{87}Sr/^{86}Sr$ of the Malvern Hills

4.2.4.1. Plant $^{87}Sr/^{86}Sr$: Set A vs. Set B

Most of the plant $^{87}Sr/^{86}Sr$ values for each of the 1km^2 boxes compare well to one another. The only exceptions are box MB1 and MB11, which have a difference of 0.0015 and 0.0011 respectively, between the mixed plant samples collected for set A vs. Set B (Figure 4.2.3). Local human populations on complicated clay and limestone bedrock can vary by ±0.002 (Evans *et al.*, 2009, p.627-628) and it is expected that bigger variances will be found in populations located on older sedimentary silicates or granitic bedrock. Therefore, a difference of approximately +0.001 between the mixed plant samples can still be seen as natural variation in the Sr-isotope value. The bedrock geology of the Malvern Hills is complex (section 4.2.1) and therefore, it was expected that there could be large range in the $^{87}Sr/^{86}Sr$ depending on the bedrocks present. The main concern however, was that the plants of set A and B were taken from the same locations within each 1km^2 box, being only a few metres apart from one another at each location.

The 1km^2 box MB1 was based on the Silurian sedimentary bedrock, specifically the Wenlock Shale and Limestone and Lower Ludlow Shale. Previous plant samples based on Silurian bedrock in Wales have recorded $^{87}Sr/^{86}Sr$ = 0.7117 ±0.0014 (n=10, 1SD) by Evans *et al.*(2010) and between 0.7097-0.7139 (Evans unpublished results; *pers.com*.). The mixed plant samples from MB1 at 0.71145 (A) and 0.70991 (B: Table 4.2.1) both compare well to these previous values on Silurian bedrock. The plants taken to create MB1 A were all tree species (oak, silver birch and a possible cherry tree), while MB1 B contained a mix of tree (sycamore) and a home cultivated 'Royal Purple' (*Cotinus coggygria:* Appendix 2). This garden shrub was chosen as, apart from the silver birch in MB1 A, no other trees were available at this location and thus was deemed the best choice. The inclusion of a garden shrub in the mixture of MB1 B may have resulted in a different, but ultimately lower^{87}Sr/^{86}Sr, because of the possible addition of fertilisers or non-local compost as well as the likelihood of being well watered (leading to saturated soils). However, as plant ^{87}Sr/^{86}Sr on Silurian bedrock can range in value quite dramatically over short distances, for example from 0.7097 to 0.7135 over 5km transect (Evans, unpublished results; *pers.com*.), the plant ^{87}Sr/^{86}Sr for MB1 could just be a reflection of this. Without re-sampling neither ^{87}Sr/^{86}Srvalue can be dismissed at present, but an improvement would be not to collect any garden plants in the future.

The 1km^2 box MB11 is on the Triassic Mercia Mudstone Group. Spiro *et al.* (2001) previously recorded water ^{87}Sr/^{86}Sr = 0.7099 ±0.0014 (n=13, 2SD) on the same bedrock. Other biosphere ^{87}Sr/^{86}Sr based on Triassic bedrock have recorded values of 0.7097 ±0.0006 (n=25, 1SD: Evans *et al.,* 2010), while the Triassic Mercia Mudstone Group in Charnwood Forest in section 4.1 has plant ^{87}Sr/^{86}Sr = 0.7119 ±0.0008 (n=3, 2SD). The plant sample MB11 A compares well to the plant samples from Charnwood Forest, at 0.71178, while MB11 B, at 0.71068, compares to the water samples in Spiro *et al.* (2001). All the plants taken to make the mixtures for MB11 A and B were from tree species and reported no unusual circumstances (Appendix, 2). As the water samples from the Mercia Mudstone Group in the Malvern Hills area ranged in value by ±0.0014 (Spiro *et al.,* 2010), the difference of +0.0011 between the mixed plant samples of MB11 is probably the result of natural variation in the ^{87}Sr/^{86}Sr value over this bedrock.

Overall the^{87}Sr/^{86}Sr results of mixing plants to produce one analytical sample over a 1km^2 area has not underlined any major problems, apart from highlighting that the collection of garden plants is best avoided because of potentially addition of fertilisers or non-local compost, as well as the likelihood of them being well watered (leading to saturated soils).

4.2.4.2. Plant $^{87}Sr/^{86}Sr$ of the Malvern Hills compared to other biosphere $^{87}Sr/^{86}Sr$ data

Previous plant $^{87}Sr/^{86}Sr$ based on the Precambrian Malvern Complex in Chenery *et al.* (2010) have recorded values of 0.71038, 0.71201, 0.71202, 0.71352 and 0.71622, while Evans (unpublished results; *pers.com*.) records a plant $^{87}Sr/^{86}Sr$ at 0.71518. The mineral water sample (JMW 07) taken from the Malvern Hills in Montgomery *et al.,* (2006) also feeds from the Malvern Complex and has an $^{87}Sr/^{86}Sr$ of 0.71329. The Precambrian Malvern Complex plant $^{87}Sr/^{86}Sr$ in this study has a mean of 0.7133 ±0.0004 (n=4, 2SD) and compares well with these previous values. Altogether the Malvern Complex can be described as having a biosphere $^{87}Sr/^{86}Sr$ = 0.7133 ±0.0031 (n=11 ,2SD: Montgomery *et al.,* 2006; Chenery *et al.,* 2010; Evans, unpublished results; this study).

The only previous plant $^{87}Sr/^{86}Sr$ on the Cambro-Ordovician bedrock had a value of 0.71508 (G-V-030: Chenery *et al.,* 2010). This value is higher compared to the values of 0.71203 (MB6 A) and 0.71286 (MB6 B) recorded from the plant $^{87}Sr/^{86}Sr$ in this study. The Silurian bedrock has previously produced plant $^{87}Sr/^{86}Sr$ of 0.70959, 0.7101, 0.71206 and 0.71292 (Chenery *et al.,* 2010; Evans, unpublished results). The most radiogenic among these values, 0.71292 (G-V-031: Chenery *et al.,* 2010), is on the May Hill Sandstone, which is the oldest Silurian formation and closest to the Precambrian Malvern Complex, while the lowest at 0.70959 is based on the Wenlock Limestone. In this study, the Silurian plant $^{87}Sr/^{86}Sr$ = 0.7105 ±0.0017 (n=10, 2SD) displays a similar trend: the highest plant $^{87}Sr/^{86}Sr$, at 0.71212 (MB5 A) and 0.71132 (MB5 B), are on May Hill Sandstone; the lowest, at 0.70974 (MB3 A) and 0.70985 (MB3 B), are on or near the Wenlock Limestone. If split, the mean plant $^{87}Sr/^{86}Sr$ = 0.7097 ±0.0003 (n=3, 2SD: Evans, unpublished results; this study) for the Silurian Wenlock Limestone and 0.7110 ±0.0021 (n=11, 2SD: Chenery *et al.,* 2010: this study) for the other Silurian sedimentary bedrock.

Water samples from the Triassic Mercia Mudstone Group, to the east of the Precambrian Malvern Complex, have recorded $^{87}Sr/^{86}Sr$= 0.7099 ±0.0014 (n=13, 2SD; Spiro *et al.*, 2001), while plant samples from Chenery *et al.* (2010) have recorded $^{87}Sr/^{86}Sr$= 0.71163 (G-V-035), 0.71418 (G-V-024) and 0.71546 (G-V-023). In this study the Triassic bedrock has recorded plant $^{87}Sr/^{86}Sr$= 0.7114 ±0.0012 (n=6, 2SD), so are higher than the water samples in Spiro *et al.* (2001), but are mostly lower than the plant values recorded by Chenery *et al.* (2010).

Chenery *et al.* (2010) discuss how the plant samples grown on or close to Quaternary head deposits around the Malvern Hills had their isotopic values strongly influenced by the source of the drift, which assumed to be the Precambrian Malvern Complex. These included the values 0.71508 (G-V-030) to the west on the Cambro-Ordovician bedrock, and the values 0.71418 and 0.71546 described above on the Triassic Mercia Mudstone Group, which lie to the east of the Malvern Complex. The Cambro-Ordovician and Triassic lithologies can also contain clasts and minerals derived from the Precambrian Malvern Complex (section 4.2.1) which may have some influence on the higher values too.

The plant samples in Chenery *et al.* (2010) were grass and herbs and there could be a possibility of 'mud-splash' on these low lying plants, leading to soil mineral contamination and higher $^{87}Sr/^{86}Sr$ values. However, the plant $^{87}Sr/^{86}Sr$ within Chenery *et al.* (2010) each involved the collection of at least two litres of vegetation per location, in which only the leaves were sub-sampled, which suggests that there was a low chance of soil contamination. Unfortunately these high values have not been able to be repeated by the plant $^{87}Sr/^{86}Sr$ in this study. The reasons for this are unknown at present and the range of values may just reflect the heterogeneous nature of the bedrock geology, as well as the possible contribution from Quaternary superficial deposits. If the two values, >0.714, based on the Triassic bedrock in Chenery *et al.* (2010) are excluded, the plant $^{87}Sr/^{86}Sr$ = 0.7114 ±0.0011 (n=7, 2SD: Chenery *et al.,* 2010; this study), if they are included it becomes 0.7122 ±0.0032 (n=9 ,2SD: Chenery *et al.,* 2010; this study).

4.2.5. Concluding remarks

Overall the method of mixing three different plants per analytical sample has not resulted in any major problems that can be seen in the $^{87}Sr/^{86}Sr$, (section 4.3 and 4.4.1). In total 33 plants have been analysed in 22 analytical samples. It has lessened the bias effect of point-sampling by collecting several plants over a given area. This can be seen in the $^{87}Sr/^{86}Sr$ values, where the plant $^{87}Sr/^{86}Sr$ in this study have not been able to reproduce the high plant $^{87}Sr/^{86}Sr$ >0.714 reported by Chenery *et al.* (2010). However, there is no reason to suggest the plant $^{87}Sr/^{86}Sr$ >0.714 reported by Chenery *et al.* (2010) are anomalous, these values are potentially just rare in the biosphere considering the heterogeneous nature of the bedrock geology. The maximum plant $^{87}Sr/^{86}Sr$ = 0.7162 (G-V-026: Chenery *et al.,* 2010) and the majority of the $^{87}Sr/^{86}Sr$ >0.714 are only found on or within 1km of the Precambrian Malvern Complex.

Sr-isotope biosphere of the Malvern Hills:

- The Precambrian Malvern Complex has a biosphere $^{87}Sr/^{86}Sr$ = 0.7133 ±0.0031 (n=11 ,2SD: Montgomery *et al.,* 2006; Chenery *et al.,* 2010; Evans, unpublished results; this study).
- The Cambro-Ordovician bedrock has a plant $^{87}Sr/^{86}Sr$ = 0.71203 (MB6 A), 0.71286 (MB6 B: this study) and 0.71508 (G-V-030: Chenery *et al.,* 2010).
- The Silurian Wenlock Limestone has a plant $^{87}Sr/^{86}Sr$= 0.7097 ±0.0003 (n=3, 2SD: Evans, unpublished results;pers.com.; this study).
- The other Silurian sedimentary bedrock has a plant $^{87}Sr/^{86}Sr$ = 0.7110 ±0.0021 (n=11, 2SD: Chenery *et al.,* 2010: this study).
- The Triassic bedrock has plant $^{87}Sr/^{86}Sr$ = 0.7114 ±0.0011 (n=7, 2SD: Chenery *et al.,* 2010; this study), as well as two elevated values at 0.71418 (G-V-024) and 0.71546 (G-V-023: Chenery *et al.,* 2010)

4.2. Tables and Figures

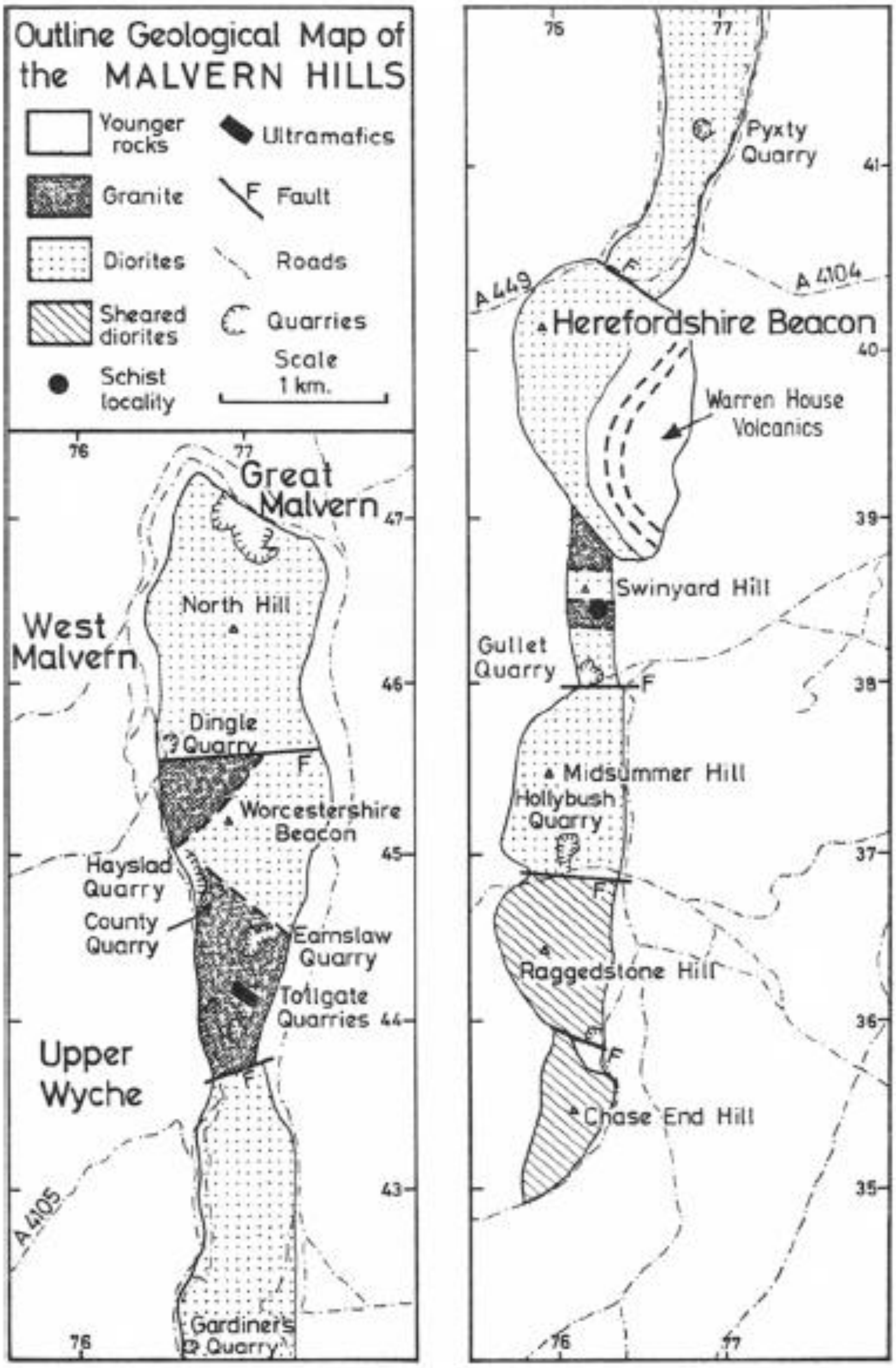


Figure 4.2.1. Figure 1 from Lambert & Holland (1971, p.329). The map shows the geology of the Malvern Hills in outline, including the principal external boundaries of the Precambrian bedrock and a few tentative internal boundaries (e.g. main fault lines and blocks of the Malvern Complex). Details of the Phanerozoic rocks surrounding, and dykes and shear-zones in the Malvern Complex are omitted. The figures around the margin indicate the 1 km. grid squares of the National Grid.

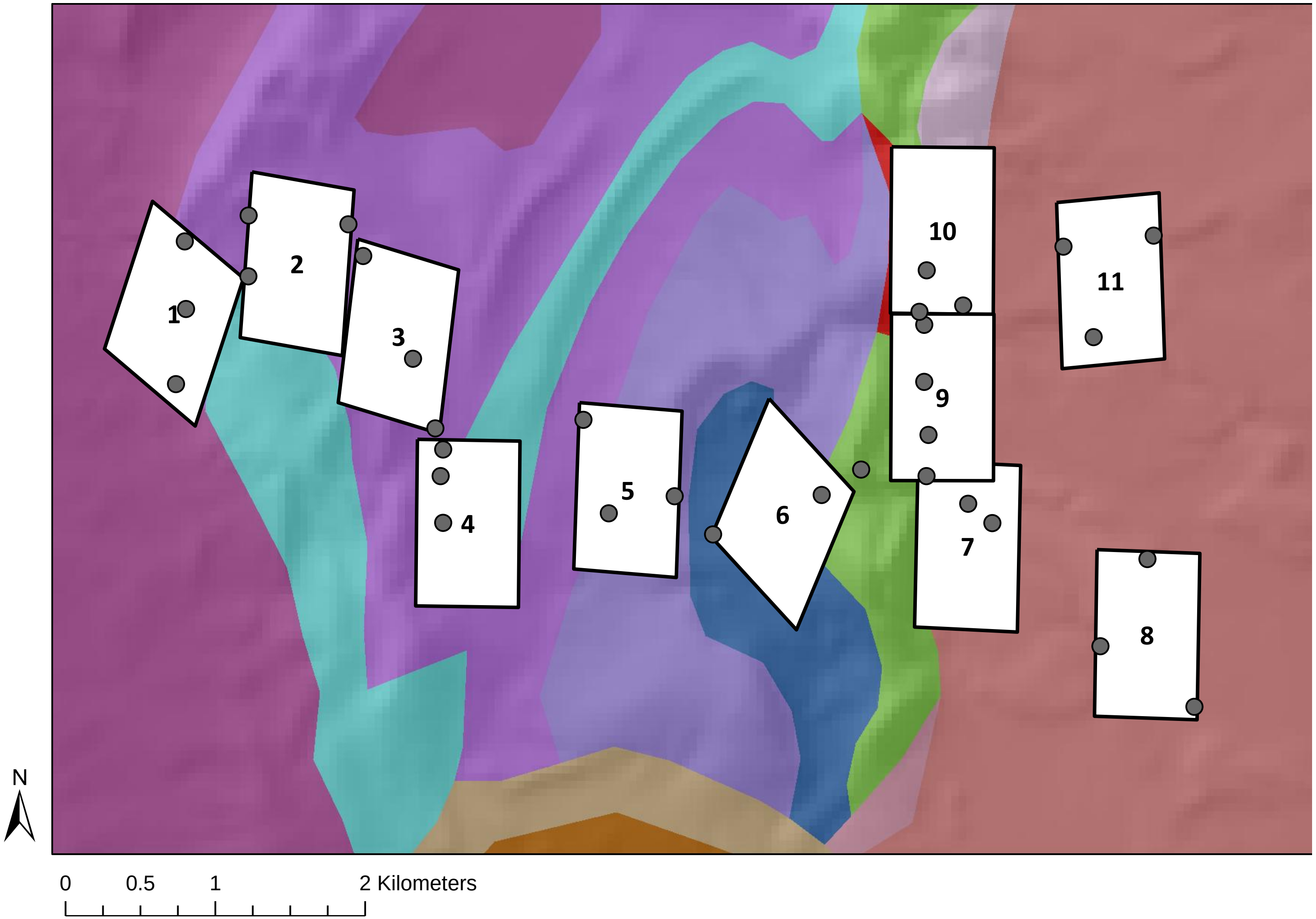


Figure 4.2.2. The position of the eleven 1km^2 'boxes' across the Malvern Hills study area (the numbered black squares) and the three locations chosen within each (grey circles), alongside GIS data of the 1:625000 Bedrock maps (BGS, DiGMapGB, 2007). The numbers match the sample code, so the 1km^{2}box labelled 1 is MB1, etc. The main legend for the Bedrock geology can be seen in Figure X.

Figure 4.2.3. The plant $^{87}Sr/^{86}Sr$ results for the Malvern Hills study area. The results for set A and B for each $1km^2$ box are displayed next to one another for comparison. For comparison against bedrock geology see Figure 4.2.4.

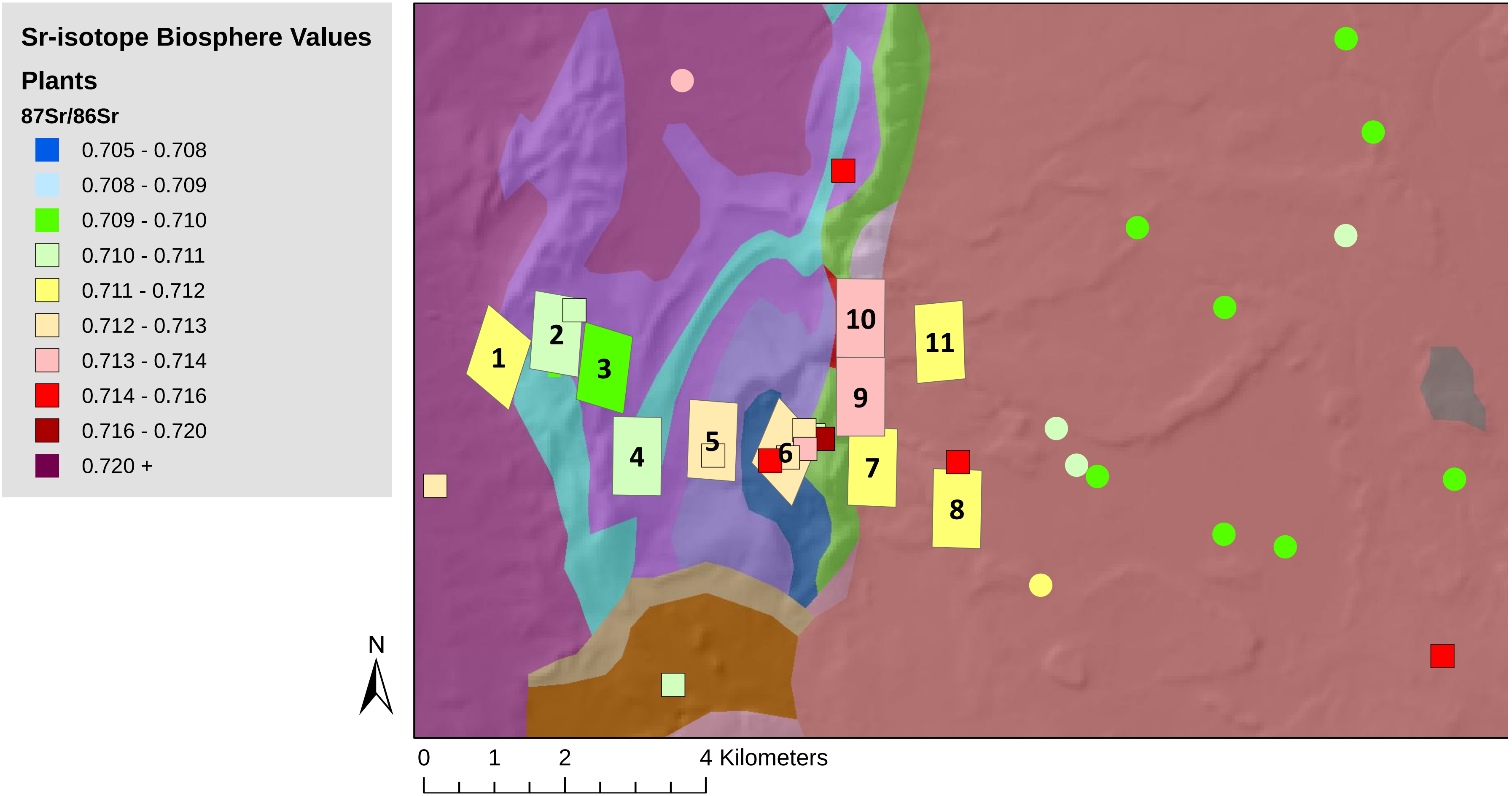
Table 4.2.1. The plant $^{87}Sr/^{86}Sr$ results for the Malvern Hills study area, along with the main bedrock geology they are based on (including age and lithologies).

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age (main Era or System)	Bedrock Lithology
MB1 A	0.71145	Silurian	Sedimentary rocks (including Limestone)
MB1 B	0.70991	Silurian	Sedimentary rocks (including Limestone)
MB2 A	0.71032	Silurian	Sedimentary rocks (including Limestone)
MB2 B	0.70973	Silurian	Sedimentary rocks (including Limestone)
MB3 A	0.70974	Silurian	Sedimentary rocks (including Limestone)
MB3 B	0.70985	Silurian	Sedimentary rocks (including Limestone)
MB4 A	0.71041	Silurian	Sedimentary rocks (including Limestone)
ML4 B	0.71041	Silurian	Sedimentary rocks (including Limestone)
MB5 A	0.71212	Silurian	Sedimentary rocks
MB5 B	0.71132	Silurian	Sedimentary rocks

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age (main Era or System)	Bedrock Lithology
MB6 A	0.71203	Cambrian; Ordovician	Sedimentary rocks
MB6 B	0.71286	Cambrian; Ordovician	Sedimentary rocks
MB7 A	0.71178	Triassic	Sedimentary rocks
MB7 B	0.71211	Triassic	Sedimentary rocks
MB8 A	0.71108	Triassic	Sedimentary rocks
MB8 B	0.71076	Triassic	Sedimentary rocks
MB9 A	0.71346	Precambrian	Igneous felsic and mafic rocks
MB9 B	0.71347	Precambrian	Igneous felsic and mafic rocks
MB10 A	0.71310	Precambrian	Igneous felsic and mafic rocks
MB10 B	0.71321	Precambrian	Igneous felsic and mafic rocks
MB11 A	0.71178	Triassic	Sedimentary rocks

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age (main Era or System)	Bedrock Lithology
MB11 B	0.71068	Triassic	Sedimentary rocks

Malvern Hills plant $^{87}Sr/^{86}Sr$: Set A



Malvern Hills plant $^{87}Sr/^{86}Sr$: Set B

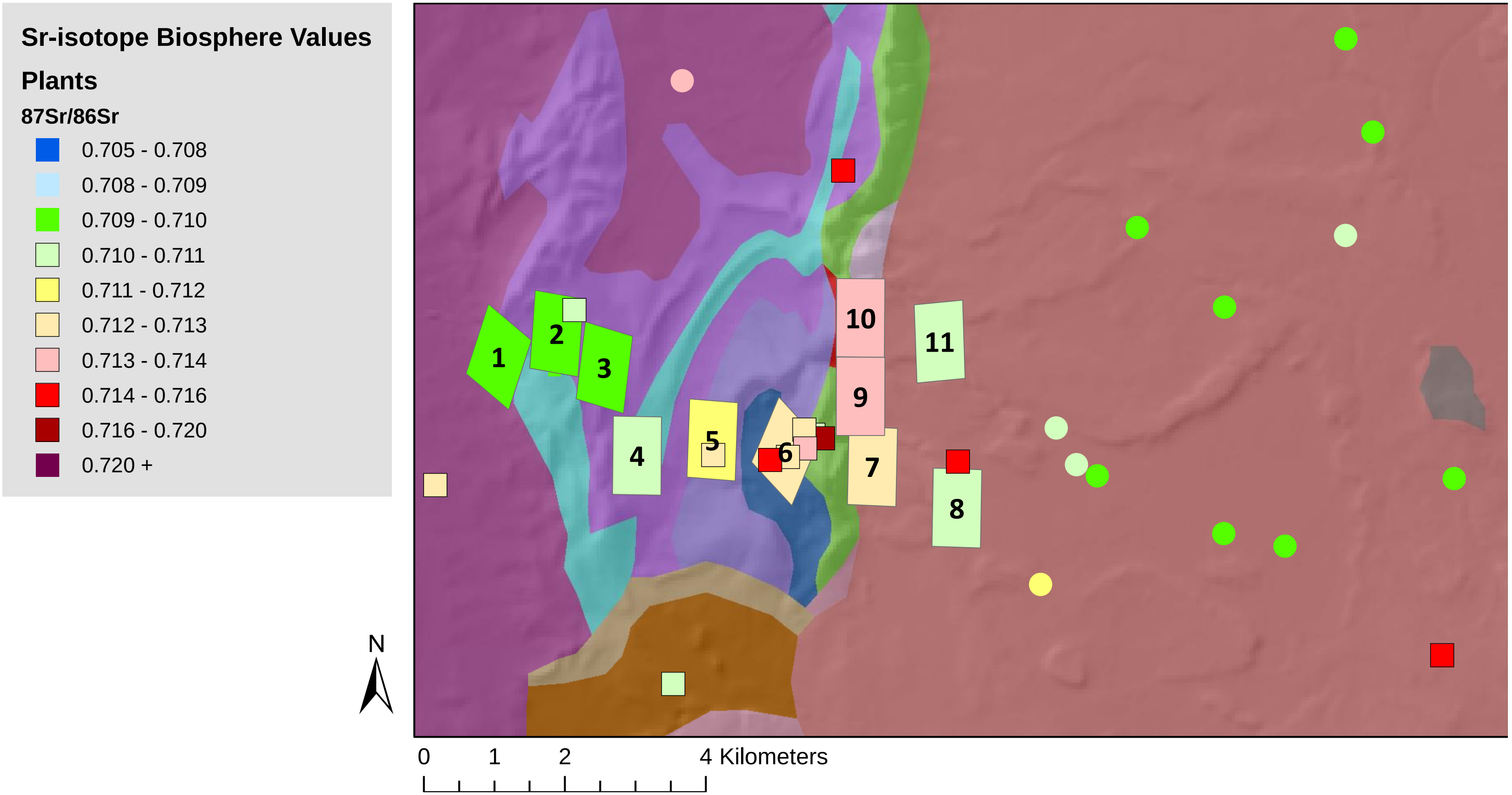


Figure 4.2.4. The plant $^{87}Sr/^{86}Sr$ results for set A (previous page) and set B (this page) for each $1km^2$ box, alongside GIS data of the 1:625000 Bedrock maps (BGS, DiGMapGB, 2007), plant $^{87}Sr/^{86}Sr$ (outlined squares) from Chenery *et al.* (2010) and Evans (unpublished results; pers.com.) and water $^{87}Sr/^{86}Sr$ (circles) from Spiro *et al.* (2001) and Montgomery *et al.* (2006). The main legend for the Bedrock geology can be seen in Figure X. The water samples (circles) has the same colour scheme as the plant samples (squares and $1km^2$ boxes).

4.3. The Sr-isotope biosphere of Nuneaton, Warwickshire, England.

Nuneaton (Figure 1.3 in chapter 1) is a town found in the county of Warwickshire, near to the borders of Leicestershire (Midlands, England). Just north-west of Nuneaton is a ~2.8km^2 Precambrian inlier, which is part of the Charnwood terrane (Pharaoh *et al.,*1987*a)*. The Charnwood terrane also includes the Precambrian inliers of Charnwood Forest (section 4.1), which are approximately 20km north of Nuneaton. The Precambrian inlier of Nuneaton is surrounded by the Carboniferous Warkwicksire Coalfields and the Triassic Mercia Mudstone Group, all of which are described further in section 4.3.1 below.

The Nuneaton study area currently has limited Sr-isotope biosphere data available. So far a plant sample taken from above Carboniferous Warwickshire Coalfields, north-west of Atherstone (~8km north-west of Nuneaton), has $^{87}Sr/^{86}Sr$ at 0.71184 (NIGL, unpublished results). There is also a dentine sample from the city of Coventry (acquired from a lady named Eliza Sparkes buried on the 31st July 1844 at Holy Trinity) on Triassic bedrock, with $^{87}Sr/^{86}Sr$ at 0.70978 (Trickett, 2007, p.215, 264). Within Trickett's doctoral thesis (2007, p.169), personal communications with Paul Budd indicated that soil leaches from the Triassic bedrock surrounding Coventry produced $^{87}Sr/^{86}Sr$ = 0.710 - 0.7115, but there was no further information regarding how these soil leaches were produced, or how many, and so they may not be the best representation of the local biosphere. This said, these soil leach values compare well with the predicted isotope package domains of 0.711-0.712 for the Carboniferous Coalfields, vs. 0.709-0.710 for the Triassic bedrock (Evans *et al.,* 2010), as well as the plant $^{87}Sr/^{86}Sr$ =0.7105 ±0.0020 (n=4, 2SD) recorded from the Carboniferous Coal Measures north of Derby, England (NIGL, unpublished results). As the Precambrian inlier of Nuneaton contained some volcanic lithologies, this study area was chosen to see if any high $^{87}Sr/^{86}Sr$ values could be found in the biosphere, as well as to complement the plant $^{87}Sr/^{86}Sr$ already recorded from Charnwood Forest, as they are both part of the Charnwood terrane.

4.3.1. Geological Summary of Nuneaton

All of the bedrock geology in the Nuneaton study area can be seen in Figure 4.3.1, alongside the plant $^{87}Sr/^{86}Sr$ for this section. The oldest bedrock geology from the Nuneaton study area is the Precambrian Caldecote Volcanic Formation. There are no longer any natural exposures of this formation and so ~100m deep sections at Judkins quarry and Boon quarry were used at the time of the geological survey (Bridge *et al.,* 1998, p.6-7). This formation consists of a succession of volcaniclastic felsic tuffs and mud-, silt- and sandstones and is intruded by several igneous rocks, also dating to the Precambrian, including basaltic-andesite, microdiorite and granophyric diorite (BGS, 1994, Sheet 169; Bridge *et al.,* 1998, p.2, 6-12). The granophyric diorite (markfieldite) that intrudes into the Caldecote Volcanic Formation has a concordant U-Pb zircon age of 603 ±2Ma, placing it in the Neoproterozoic. This date is considered the most reliable isotopic age constraint on Charnian magmatism and is in assumed lithological correlation with the southern diorites of Charnwood Forest (Pharaoh & Gibbons, 1994).

Cambrian lithologies then rest unconformably to the west of the Precambrian bedrock above, and together they are referred to as the Precambrian or Nuneaton inlier (even though some of the lithologies are in the Palaeozoic). The Cambrian lithologies here are one of the most extensive and complete Cambrian sequences found in Britain and commences with the Harthill Sandstone Formation of the Comley Series (Lower Cambrian), which includes varying sandstones with some mudstones and breccia. This formation is then followed by the Stockingford Shale Group (Middle to Upper Cambrian), containing several series of mainly varying mudstones with some silt- and sandstone beds (BGS, 1994, Sheet 169; Bridge *et al.,* 1998, p.2, 21-37).

The northern section of the Cambrian bedrock is overstepped by an 2.5km long outcrop of Devonian rocks, which are part of the Oldbury Farm Sandstone Formation, consisting of grey-green conglomerates, sand and siltstones and reddish brown to green silty and sandy mudstones. These are in turn overstepped by a slither of coarse-grained sandstones of the Millstone Grit Group of the Carboniferous (BGS, 1994, Sheet 169; Bridge *et al.,* 1998, p.50).

The southern section of Cambrian bedrock on the other hand is immediately overstepped by the Carboniferous rocks of the Warwickshire Coalfields (Bridge *et al*., 1998, p.21). The Warwickshire Coalfields are bounded to the west by the Western Boundary Fault System and by the Triassic bedrock to the north-east and south-east. Starting from the Nuneaton inlier and heading westward, the Warwickshire Coalfields include: the Pennine Coal Measures, a succession of varying sedimentary rocks with many coal seams; the Barren Measures, a very thick succession (~1000m) of predominantly red mudstones and sandstones, with subordinate lenticular conglomerates and limestones (BGS, 1994, Sheet 169; Bridge *et al.,* 1998, p.2, 57-61,71-72).

To the east of the Nuneaton inlier a great unconformity is formed as Triassic bedrock overlaps westwards across the Polesworth Fault and onto the Precambrian bedrock. The Triassic lithologies in this study are either part of the Sherwood Sandstone Group or the Merica Mudstone Group and are confined to the Hinckley Basin, a fault-bounded trough that formed during the Late Permian to early Triassic (Bridge *et al.,* 1998, p.6, 87). The Sherwood Sandstone Group (in which only the uppermost Bromsgrove Sandstone is present as an outcrop) consists mainly of red, yellow and brown sandstones interbedded with conglomerates. They are indicative of fluvial origins and are followed conformably by the Mercia Mudstone Group (Warrington *et al.,* 1980; BGS, 1994, Sheet 169; Bridge *et al.,* 1998, p87-88, 92). The Mercia Mudstone Group is comprised of formations that are argillaceous in nature (containing lots of clay minerals) being dominated by red mudstones which are often referred to as 'red beds', but also contain subordinate siltstones with thick halite-bearing units in some basinal areas. The majority of the 'red beds' were deposited through wind action in subaqeuous playas or inland sabkha environments (Warrington *et al.*, 1980; Bridge *et al.,* 1998, p.87, 92-95; Carney, 2010).

The majority of the Quaternary superficial deposits in and around Nuneaton are of glacial origin. They are mainly part of the Wolston Glacial Succession (dating to the Anglian), but also include smaller areas of late glacial or post-glacial deposits, like the river terrace deposits and alluvium. They form thick coverings over the Triassic bedrock to the east, starting patchy with the Anker sand and gravel, river terrace deposits and alluvium around Nuneaton and moving eastwards into continuous cover of the Wolston Glacial Succession (being up to 80m thick in some areas). The Wolston Glacial Succession can contain a variety of erratics, many obtained locally but also include the Leicestershire granodiorites, ironstones from Carboniferous Coal measures and Lower Carboniferous limestones (Bridge *et al.,* 1998, p.102). Superficial deposits, mainly till, are much more patchy over the Nuneaton inlier and the Warwickshire Coalfields, with larger deposits being found to the south heading towards the market town of Bedworth (BGS, 1994, Sheet 169; Bridge *et al.,* p.98-117).

4.3.2. Geochemical Survey and Field-notes for Nuneaton

In September 2015 a total of eight locations were visited across Nuneaton. The weather over the collection period was sunny with cloudy spells. The plant samples were collected and mixed for each location by the main methods described in chapter 3, section 3.2. The field-notes for the mixed plant samples from across Nuneaton can be viewed in the Appendix 2. These plant samples followed the same methods for chemical preparation and Sr-isotope analysis outlined in section 3.3 in chapter 3.

4.3.3. Plant $^{87}Sr/^{86}Sr$ Results and Discussion

The plant $^{87}Sr/^{86}Sr$ from across the Nuneaton study area can be seen in Figure 4.3.1 and 4.3.2. No $^{87}Sr/^{86}Sr$ >0.714 have been produced and instead all of the mixed plant samples from across the Nuneaton study area have plant $^{87}Sr/^{86}Sr$ = 0.7108 ±0.0016 (n=8, 2SD). If separated by bedrock, the Nuneaton inlier (including Precambrian and Cambrian lithologies) have plant $^{87}Sr/^{87}Sr$ = 0.70989 (NUN L3) and 0.71045 (NUN L4), the Carboniferous Warwickshire Coalfields have 0.7112 ±0.0023 (n=3, 2SD) and the sedimentary rocks of the Triassic have 0.7109 ±0.0011 (n=3, 2SD). Even though there are volcanic tuffs of felsic composition within the Precambrian Caldecote Volcanic Formation, it is mainly a formation of sedimentary rocks (section 4.3.1) and this is expected to result in a lower $^{87}Sr/^{86}Sr$ contribution overall; a similar situation has been discussed with the Precambrian Charnian Supergroup of Charnwood Forest (section 4.1). The Precambrian part of the inlier is also very small (~2.8km^2) and is not exposed. So even if high $^{87}Sr/^{86}Sr$ values were released from the Precambrian bedrock they would have to compete and dominate all the other $^{87}Sr/^{86}Sr$ values released from geological bedrocks of the Carboniferous and Triassic, as well as atmospheric Sr and any other Sr inputs into the biosphere. This clearly has not happened and instead the lowest plant $^{87}Sr/^{86}Sr$ in the Nuneaton study area, at 0.70989 (NUN L3) is found upon the inlier.

The Carboniferous Warwickshire Coalfields can be split between the Pennine Coal Measures and the Barren Measures (see section 4.3.1 for geological descriptions). The Pennine Coal Measures, which overstep the Nuneaton inlier to the south, have plant $^{87}Sr/^{86}Sr$ = 0.71035 (NUN L7) and 0.71067 (NUN L5), while the Barren Measures have plant $^{87}Sr/^{86}Sr$ = 0.71249 (NUNL6) and 0.71184 (NIGL, unpublished results). The latter value from the plant sample JMPD_20 (NIGL, unpublished results) was taken very close to the boundary between the Pennine Coal Measures and Barren Measures and is situated approximately 2km north of the Nuneaton inlier (Figure 4.3.1). The mixed plant sample NUN L6 was also over 2km away from the Nuneaton inlier. This suggests that, considering the proximity to the Nuneaton inlier, the plant $^{87}Sr/^{86}Sr$ on the Pennine Coal Measures could be influenced by the weathering of the Nuneaton inlier, resulting in a lower $^{87}Sr/^{86}Sr$ than found further north and west on the Warwickshire Coalfields. Overall though, the plant $^{87}Sr/^{86}Sr$ produced from the Carboniferous Warwickshire Coalfields compare well with the predicted isotope package domain of the 0.711-0.712 for the Carboniferous Coalfields (Evans *et al.,* 2010) and the plant $^{87}Sr/^{86}Sr$ = 0.7105 ±0.0020 (n=4, 2SD) already recorded from the Carboniferous Coal Measures north of Derby, England (NIGL, unpublished results).

The Triassic bedrock consists of the Sherwood Sandstone Group and the Mercia Mudstone Group (see section 4.3.1 for geological descriptions). The plant $^{87}Sr/^{86}Sr$ on the Sherwood Sandstone group has a value of 0.71032 (NUN L8). This mixed plant sample is also in close proximity to the Nuneaton inlier (<1km). Altogether, the $^{87}Sr/^{86}Sr$ for plants collected on and within approximately 1km of the Nuneaton inlier have an mean value of 0.7103 ±0.0006 (n=5, 2SD). However, as only one mixed plant sample was taken from the Sherwood Sandstone Group it is hard to state whether the plant $^{87}Sr/^{86}Sr$ is a result of Sr input from the Nuneaton inlier and the Triassic lithologies or purely reflective of the Triassic Sherwood Sandstone Group.

The plant $^{87}Sr/^{86}Sr$ from the Triassic Mercia Mudstone Group, at 0.71110 (NUN L1) and 0.71140 (NUN L2), are higher than the Triassic biosphere $^{87}Sr/^{86}Sr$ = 0.7097 ±0.0006 (n=24, 1SD), reported in Evans *et al.* (2010). The plant $^{87}Sr/^{86}Sr$ in this study are higher by a minimum of 0.0014. A similar observation was made for plant $^{87}Sr/^{86}Sr$ based on the Mercia Mudstone Group in Charnwood Forest, which were also higher by approximately

0.0022 (section 4.1). As at Charnwood Forest, the plants used to create these two mixed plant samples (NUN L1 and NUN L2) were collected from woodland (Appendix 2) and perhaps may be influenced by the woodland effect (see chapter 2, section 2.4.3). It would be interesting to see if this trend continues, both when collecting plant $^{87}Sr/^{86}Sr$ from Triassic bedrock and from woodland environments.

4.3.4. Concluding remarks

Overall the mixed plant samples across the Nuneaton study area have not recorded any values >0.714. The Sr-isotopes biosphere of this area at present is as follows:

- The Nuneaton inlier (including Precambrian and Cambrian lithologies) has plant $^{87}Sr/^{87}Sr$ = 0.70989 (NUN L3) and 0.71045 (NUN L4). All mixed plant samples on and within 1km of the Nuneaton inlier have $^{87}Sr/^{86}Sr$ = 0.7103 ±0.0006 (n=5, 2SD).
- The Carboniferous Warwickshire Coalfields, the Pennine Coal Measures have plant $^{87}Sr/^{86}Sr$ = 0.71035 (NUN L7) and 0.71067 (NUN L5).
- The Carboniferous Warwickshire Coalfields, the Barren Measures have plant $^{87}Sr/^{86}Sr$ = 0.71249 (NUNL6) and 0.71184 (NIGL, unpublished results).
- The Triassic Sherwood Sandstone Group has a plant $^{87}Sr/^{87}Sr$ =0.71032 (NUN L8).
- The Triassic Mercia Mudstone Group has plant $^{87}Sr/^{87}Sr$ = 0.71110 (NUN L1) and 0.71140 (NUN L2).

4.3. Figures

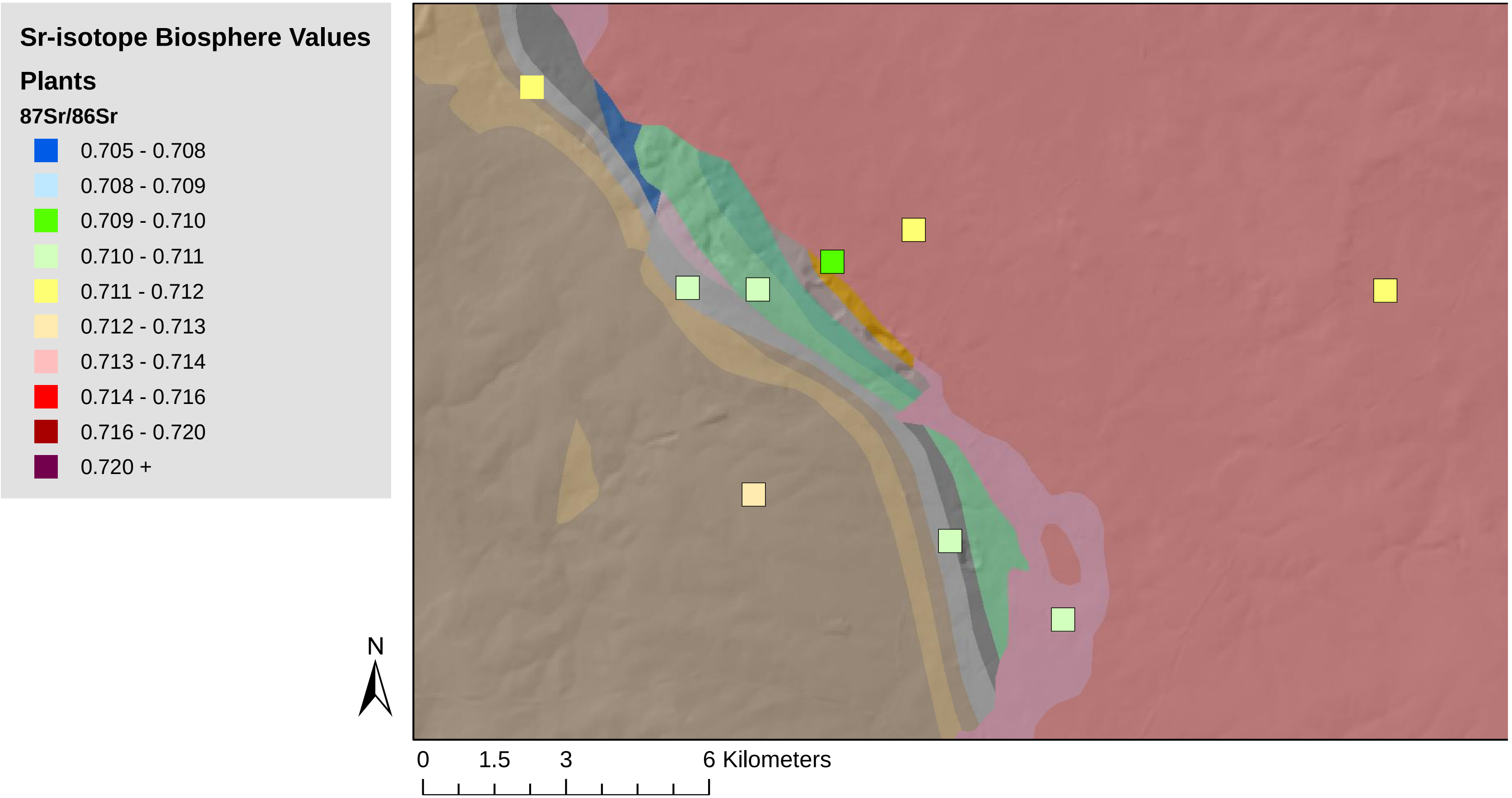


Figure 4.3.1. The plant $^{87}Sr/^{86}Sr$ (outlined squares) from across the Nuneaton study area, alongside GIS data of the 1:625000 Bedrock maps (BGS, DiGMapGB, 2007). The main legend for the Bedrock geology can be seen in Figure X. The single plant sample (represented by the square not outlined) is JMPD_20 (NIGL, unpublished results).

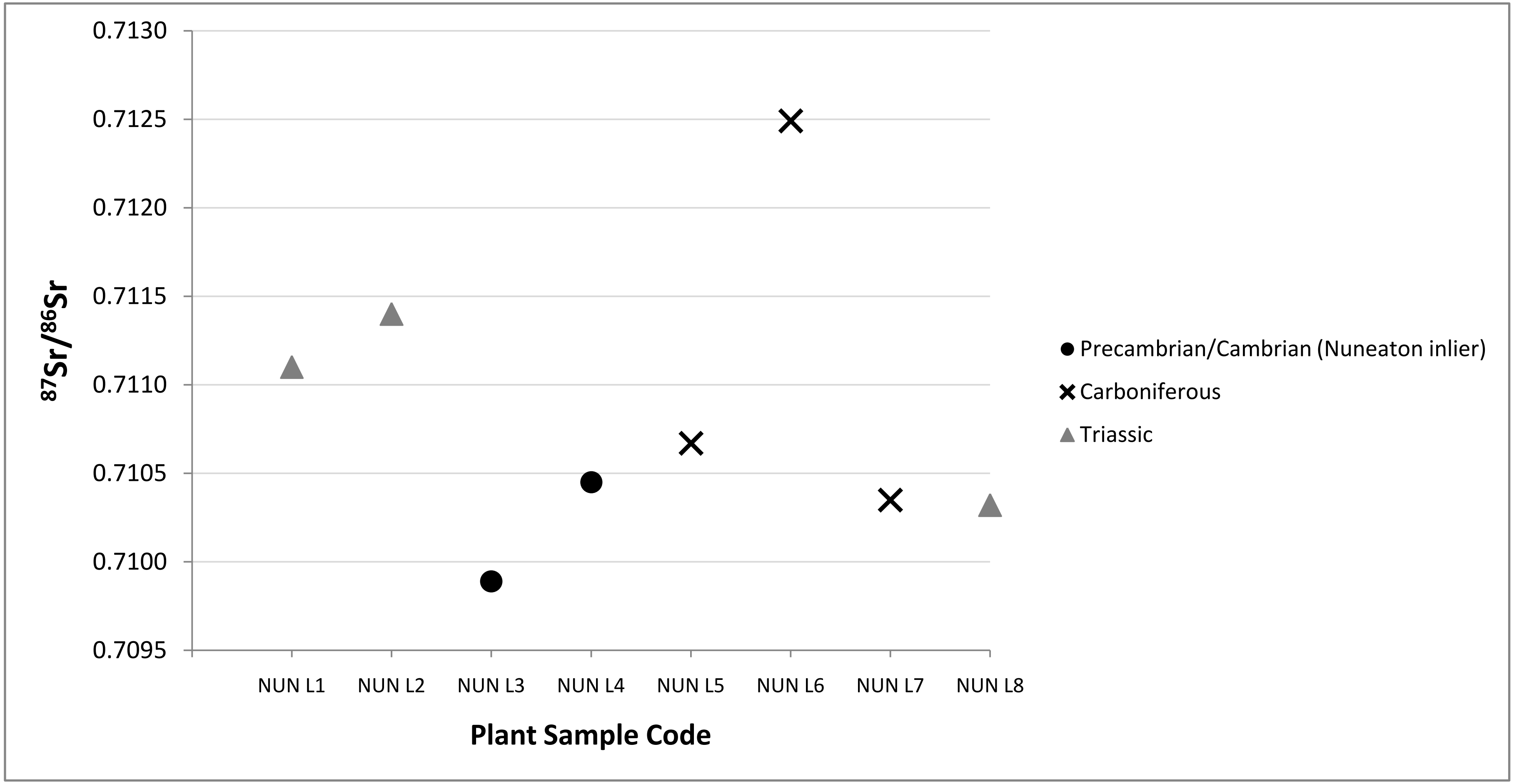


Figure 4.3.2. The plant $^{87}Sr/^{86}Sr$ results from across the Nuneaton study area, based on the age of the main bedrock geology from which they were taken.

4.4. The Sr-isotope biosphere of Church Stretton

The town of Church Stretton is found in the county of Shropshire, approximately 10km east of the Wales Border (Figure 1.3 in chapter 1). The area surrounding this town is home to the largest Precambrian outcrops found in England. They form the majority of Long Mynd, an isolated whaleback hill protected by the National Trust, and the Stretton Hills on the eastern side of Church Stretton. The Precambrian bedrock found here, along with those at the Wrekin (Shropshire: section 4.5) and the Stanner-Hanter Complex (Herefordshire: section 4.6), all occur within and to the east of the Welsh Borderlands Fault System (Pharaoh & Gibbons, 1994). The bedrock geology of Church Stretton dates from the Precambrian through to the Carboniferous, although for the purpose of this study only the underlying bedrock from which plant samples were collected are described below in the geological summary (section 4.4.1). Quaternary superficial deposits are also common in this area (Greig *et al.*, 1968, p.1-8; Toghill, 1990, p.9-16) as it was near to the extent of the last glacial ice sheet in Britain (Clark *et al*., 2004; Evans *et al.,* 2005; Clark *et al.,* 2017).

To date, the nearest Sr-isotope biosphere samples lie to the west of the Church Stretton study area and are all based on Silurian sedimentary bedrock. They include three mineral water samples, located about 1km south-west of Cordon Hill (which lies on the Welsh Border: Montgomery *et al.,* 2006) and three plant samples between 10-20km west to south-west of Cordon Hill (Evans *et al*., 2010). The water $^{87}Sr/^{86}Sr$ = 0.71169, 0.71178 and 0.71192 (Montgomery *et al.,* 2006) and the plant $^{87}Sr/^{86}Sr$ = 0.71299, 0.71137 and 0.70999 (Evans *et al.,* 2010). No Sr-isotope biosphere data are available from on the Precambrian bedrock in and around Church Stretton.

4.4.1. Geological Summary of Church Stretton

The bedrock geology of the Church Stretton study area can be seen in Figure 4.4.1 and the Quaternary superficial deposits in Figure 4.4.2.

The Precambrian bedrock is either part of the Uriconian, predominately igneous rocks of volcanic origin, or the Longmyndian, a very large succession of sedimentary rocks (Greig *et al.*, 1968, p.1-8; Toghill, 1990,p.9-16). The Uriconian, forming the Stretton Hills, contain a variety of igneous felsic and mafic volcanic lithologies including tuffs, rhyolites, andesites, dacites and basalts. They are the oldest rocks in this area, which are believed to date to the Neoproterozoic based on the U-Pb zircon, Rb-Sr whole-rock isochron and whole-rock K-Ar ages of other Uriconian outcrops in England and Wales (dates ranging from 560 ±1Ma to 677 ±72Ma: Pharaoh & Gibbons, 1994). These volcanic lithologies are then succeeded by the Longmyndian, which forms the majority of the Long Mynd. The Longmyndian can be divided into the older Stretton Series, which can vary from purple to greenish grey mud, silt and sandstones, some of which are micaceous (the Cardingmill Grit in the Burway Group) and can contain volcanic tuff horizons (within the Synalds Group and Stretton Shale Group) and the younger Wentor Series, a series of purple mud, silt and sandstones with occasional gritstones and conglomerates. The Precambrian lithologies of the Stretton Hills and Long Mynd are bought into contact with the younger bedrock of the Ordovician and Silurian mainly through the Church Stretton Fault Complex (Greig *et al.,* 1968, p.1-8, 10-92; BGS, 1980, Sheet 166; Toghill, 1990, p.24-28, 29-40).

Separated by an unconformity, the Cambrian succession oversteps the Precambrian Longmyndian succession. Split by age and undivided on the Sheet 166 1:50000 series map, the Lower Cambrian contains the older Wrekin Quartzite and the younger Lower-Comley Series (mainly sandstones and thin limestones: Greig *et al.*, 1968, p.3, 93-4; BGS, 1980, Sheet 166). The Middle Cambrian contains the Upper-Comley Series with various shales, gritstones and sandstones. Finally, the Upper Cambrian contains the older Dolgelly Beds (grey and black shales, although it was doubted whether the black shales are present in this area) and the Tremadoc Series, again mainly shales, which leads into the Ordovician period.

Another unconformity separates the Cambro-Ordovician Tremadoc Series above, from the purely Ordovician lithologies to the east of the Church Stretton Fault Complex. These are part of the Caradoc Series, which contains a variety of sandstones, mudstones and siltstones. Conglomerates can be found in the oldest group in the Ordovician Caradoc Series, the Hoar Edge Grit, while many of the other groups can contain thin limestone beds and a lot of the mudstones are described as micaceous (Greig *et al.,* 1968, p.3, 102-117; Toghill, 1990, p.77-81).

To the west of the Church Stretton Fault Complex, the Cambro-Ordovican Tremadoc Series lithologies lie in fault contact with the Precambrian Longmyndian succession of Long Mynd (Pontesford Linley Fault). Passing west still, is the Ordovician Arenig Series, with only the Stiperstones Quartzite Formation, the Mytton Flags Formation (mainly silt and sandstones) and the Hyssington Volcanic Member (mainly felsic tuffs and volcaniclastic sandstones) being important for this study. Just over 1km to the west is the Ordovician igneous mafic intrusion of Cordon Hill (mainly dolerite), although not directly sampled from this outcrop may influence the biosphere in this area (BGS, 1994, Sheet 165; Toghill, 1990, p.64-70, 74-75).

The Ordovician lithologies in this area are rich in lead-zinc and barytes mineralisation that form in hydrothermal veins ranging in size from 1cm to 3-5m across (possibly indicating a large granite intrusion yet to be discovered, approximately 5-10km under the surface: Toghill, 1990, p75-77). Furthermore the bedrocks of the Precambrian Uriconian and Longmyndian, Cambrian and some of the Ordovician rocks to the west of the Church Stretton Fault Complex are also cut by many igneous intrusions believed to date to the late Ordovician. They are mainly small 3m thick dolerite dykes, but can vary in thickness from 1 - 60m (Greig *et al.,* 1968, p.53).

The Silurian lithologies then follow, being mainly a succession of varying sedimentary rocks including limestone. In this area only the older Llandovery Series (Upper), Wenlock Series and Ludlow Series to the east of the Church Stretton Fault Complex are sampled from (or in close proximity to sample location) and are brought into contact with the older Precambrian lithologies through mainly the Church Stretton Fault Complex. The Llandovery Series contains sandstones and shales mainly (with thin limestone beds), the Wenlock Series contains calcareous mudstones, calcareous siltstones and limestones (some are argillaceous) and the Ludlow series contains mainly mud and siltstones with some argillaceous limestones (Greig *et al*., 1968, p.2-3, 141-144; Toghill, 1990, p.92-94, 96). The Siluro-Devonian Old Red Sandstone (ORS) can be found further east, over 10km away from Church Stretton (Greig *et al.,* 1968, p.2, 7; BGS, 1980, Sheet 166), but was not sampled from in this study as all previous work has indicated this lithology produces biosphere $^{87}Sr/^{86}Sr$ below 0.714 (Evans *et al.,* 2010; Evans *et al.* 2012).

Just to the north of the Precambrian bedrock of Church Stretton and Long Mynd, heading towards the large village of Dorrington, Shrewsbury, Carboniferous bedrock overlies the older lithologies. Plant samples were only taken south of Dorrington, from above the Halesowen Formation which are mainly coal-bearing mud-, silt- and sandstones (BGS, 1978, Sheet 152;BGS, 2007, South). This was the youngest bedrock geology in this study area.

The Quaternary superficial deposits in the Church Stretton area include glacial till, head deposits and sand and gravels, as well as post-glacial river terrace deposits and alluvium. The glacial till deposits and the post-glacial alluvium (with some sand and gravel deposits) are mainly found in the Church Stretton Horderley Valley and further to the west past Long Mynd. The head deposits lie towards the north-west on the Long Mynd and the majority of the glacial sand and gravel and river terrace deposits are to the north, towards the large village of Dorrington. All are mainly derived from the local rocks, but the till deposits have been recorded to contain erratics of non-local origin, such as granites from Scotland and Lake District and dolerite similar to those found in Breidden Hill, Powys, Wales (Greig *et al*., 1968, p.1, 282-284;BGS, 1967, Sheet 166, Drift; Toghill, 1990, p.167-179)

4.4.2. Geochemical Survey and Field-notes for Church Stretton

In September 2015 a total of 13 locations were visited across the Church Stretton area (mainly between the Stretton Hills and Cordon Hill). The weather over the collection period was mainly cloudy but dry with some sunny periods. The plant samples were collected and mixed for each location by the main methods described in Chapter 3, section 3.2. The field-notes for the mixed plant samples from across the Church Stretton can be viewed in the Appendix 2 and they followed the same methods for chemical preparation and Sr-isotope analysis outlined in section 3.3 in Chapter 3.

4.4.3. Plant $^{87}Sr/^{86}Sr$ Results and Discussion

The plant $^{87}Sr/^{86}Sr$ results from across the Church Stretton study area are displayed in Figure 4.4.3. They are also displayed alongside the bedrock geology and Quaternary superficial deposits of the Church Stretton study area in Figure 4.4.1 and 4.4.2

respectively. The plant samples collected from Precambrian bedrocks, including both the Uriconian and the Longmyndian lithologies, have a plant $^{87}Sr/^{86}Sr$ = 0.7116 ±0.0003 (n=5, 2SD). The sedimentary rocks of the Ordovician Arenig Series have a plant $^{87}Sr/^{86}Sr$ at 0.71220 (CS L1), while the felsic tuffs of the Hyssington Volcanic Member, of the same series, have a plant $^{87}Sr/^{86}Sr$ at 0.71406 (CS L2). The sedimentary rocks of the Ordovician Caradoc Series have a plant $^{87}Sr/^{86}Sr$ at 0.71246 (CS L9).

The Silurian sedimentary rocks to the east of Church Stretton have a plant $^{87}Sr/^{86}Sr$ at 0.70942(CS L7), which was the lowest biosphere value for the study area. It is similar, albeit slightly less radiogenic, to the plant sample FISH-2, at 0.70999 (Evans *et al*. 2010), also on Silurian bedrock, but approximately 30km to the west. The Carboniferous bedrock of the Halesowen Formation (coal-bearing sedimentary lithologies) to the north of Church Stretton and Long Mynd have plant $^{87}Sr/^{86}Sr$ at 0.71248 (CS L5) and 0.71374 (CS L6). The first Carboniferous value compares well to the Carboniferous Grits of south Devon, with water $^{87}Sr/^{86}Sr$ = 0.7126 ±0.0001 (n=4, 1SD; Evans *et al.,* 2010) and plant $^{87}Sr/^{86}Sr$ ranging between 0.71065-0.71283 on the Carboniferous Coal Measures of the Midlands (NIGL unpublished results: see chapter 2, section 2.3.1 for main description). The second value is the most radiogenic biosphere value currently taken from Carboniferous bedrock in England and so is considered an anomaly.

There are three samples that have been excluded from the discussion and calculations above, as they have unusually high $^{87}Sr/^{86}Sr$ ratios for southern Britain. These are discussed below in more detail.

4.4.3.1. The aureole of high plant $^{87}Sr/^{86}Sr$

The Church Stretton study area produced three plant samples that have no obvious lithological reason for their high $^{87}Sr/^{86}Sr$ values. The plant sample CS L3 (0.71524) and CS L12 (0.71536) are based on the Precambrian Longmyndian and Ordovician Caradoc Series respectively, both consisting of mainly sedimentary rocks. These two values line up with CS L2, located on the Ordovician felsic tuffs of the Arenig Seires (0.71406), making a south-east to west transect of plant $^{87}Sr/^{86}Sr$ >0.714 (Figure 4.4.1). Then there is CS L6 (0.71374), on the Carboniferous bedrock. Samples CS L6 and CS L12 were collected from woodland (Appendix 2), therefore their $^{87}Sr/^{86}Sr$ values could be more radiogenic due to the woodland effect (chapter 2, section 2.4.3). However, this does not explain CS L3 which was taken from tree verges surrounded by agricultural land.

The positions of these unusually high plant $^{87}Sr/^{86}Sr$ are interesting as they are all found at low elevations. Sample CS L6 is found in the lower valley north of the Stretton Hills, while CS L3 and CSL12 are both found on the southern edges of the Long Mynd and Stretton Hills, which line up with CS L2 described above (Figure 4.4.1). Together they form a aureole around the base of Precambrian bedrock of the Uriconian and the Longmyndian.

It is hypothesised that CS L6 could reflect the weathering of the Stretton Hills northwards, while CS L3 and CS L12 could be a result of weathering of the Long Mynd and Stretton Hills southwards. The plant $^{87}Sr/^{86}Sr$ may be more radiogenic in value to the south because the extent of the last glacial ice sheet in Britain was not far from this position (Clark *et al*., 2004; Evans *et al.,* 2005; Clark *et al.,* 2017), so the southern end of Long Mynd and Stretton Hills potentially has experienced greater weathering and erosion as the ice sheet advanced and retreated. Figure 4.4.2 shows the extent of the last glacial ice sheet (white dashed line: Clark *et al*., 2004; Evans *et al.,* 2005; Clark *et al.,* 2017) alongside the plant $^{87}Sr/^{86}Sr$ from across the Church Stretton study area. The transect of high plant $^{87}Sr/^{86}Sr$ runs approximately south-east to west, which follows a similar direction to the moraine deposits (Figure 4.4.2: Clark *et al*., 2004; 2017). The moraine deposits (lines and polygons in Figure 4.4.2) from Clark *et al*. (2004; 2017) include any ice-marginal accumulations of sediment with a topographic expression defining a distinct landform (not just sheet-like spreads as displayed by the BGS 1:625,000 Superfical Geology Map, 1997). They usually comprise glacial till but in the definition by Clark *et al*. (2004; 2017) also include ice-contact fans that contain fluvially deposited sand and gravels (e.g. glacial sand and gravels). If they contain weathered and eroded material that has high $^{87}Sr/^{86}Sr$,, which could possibly be from the Precambrian bedrock, the biosphere $^{87}Sr/^{86}Sr$ may reflect this.

Clark *et al.* (2017) also records the transport direct of erratic boulders from the Eskdale granite, which originates from the Eskdale Pluton in the Lake District (black line with arrow: Figure 4.4.2). The extent of their transport ends just to the east of the Stretton Hills and close to the extent of the last glacial ice sheet (white dashed line: Figure 4.4.2). Presently, the Eskdale granite have a whole-rock $^{87}Sr/^{86}Sr$ between 0.72436 - 1.11430, averaging at 0.95715 (n=10: Rundle, 1979) and 0.91373 (chapter 7, section

7.5.1), while plant samples taken from above the same pluton have $^{87}Sr/^{86}Sr$ at 0.71053 (LD L9) and 0.71298 (LD L17: section 4.7). The plant biosphere on the Eskdale Pluton is not as radiogenic as expected considering its granitic nature and whole-rock $^{87}Sr/^{86}Sr$. However, the Lake District experiences a high annual average of rainfall >1250 to >3000mm (Met Office, Rainfall amount Annual Average map, 1981-2010) and so these values are believed to be influenced heavily by atmospheric Sr (~0.7092: Veizer, 1989, p.142). If a large amount of material from the Eskdale granite is also present in the moraine and till deposits on the southern end of Long Mynd and the Stretton Hills, they may contribute to the more radiogenic values seen considering the whole-rock $^{87}Sr/^{86}Sr$ of the Eskdale granite, as well as the fact that the annual average of rainfall for Church Stretton is much less than seen in the Lake District, at 800-1000mm (Met Office, Rainfall amount Annual Average map, 1981-2010). Again though, this hypothesis may only explain the high plant $^{87}Sr/^{86}Sr$ to the north of the Long Mynd and Stretton Hills, at 0.71374 (CS L6), which is within the transport pathway of the Eskdale erratics, but not the values to the south, which are approximately 10km away (Figure 4.4.2). Future sampling of the plant $^{87}Sr/^{86}Sr$ from around the Precambrian bedrock in the Church Stretton area would be beneficial to see if this aureole of high values continues.

4.4.4. Concluding remarks

Three samples from the Church Stretton study area have $^{87}Sr/^{86}Sr$ values >0.714 (CS L2, CS L3 and CS L12). Together, along with another sample at 0.71374 (CS L6), they form a biosphere aureole around the base of the Precambrian Uriconian and Longmyndian. All other plant $^{87}Sr/^{86}Sr$ compare well to the bedrock they are based on and so the Sr-isotope biosphere of Church Stretton is as follows:

- The Precambrian Uriconian and Longmyndian have plant $^{87}Sr/^{86}Sr$ =0.7116 ±0.0003 (n=5, 2SD).
- The sedimentary rocks of the Ordovician Arenig Series has a plant $^{87}Sr/^{86}Sr$ = 0.71220 (CS L1).
- The felsic tuffs of the Ordovician Arenig Series has a plant $^{87}Sr/^{86}Sr$ = 0.71406 (CS L2).

- The sedimentary rocks of the Ordovician Caradoc Series has a plant $^{87}Sr/^{86}Sr$ = 0.71246 (CS L9).
- The Silurian sedimentary bedrock has a plant $^{87}Sr/^{86}Sr$= 0.70942(CS L7).
- The Carboniferous Halesowen Formation has a plant $^{87}Sr/^{86}Sr$ = 0.71248 (CS L5).

4.4 Figures

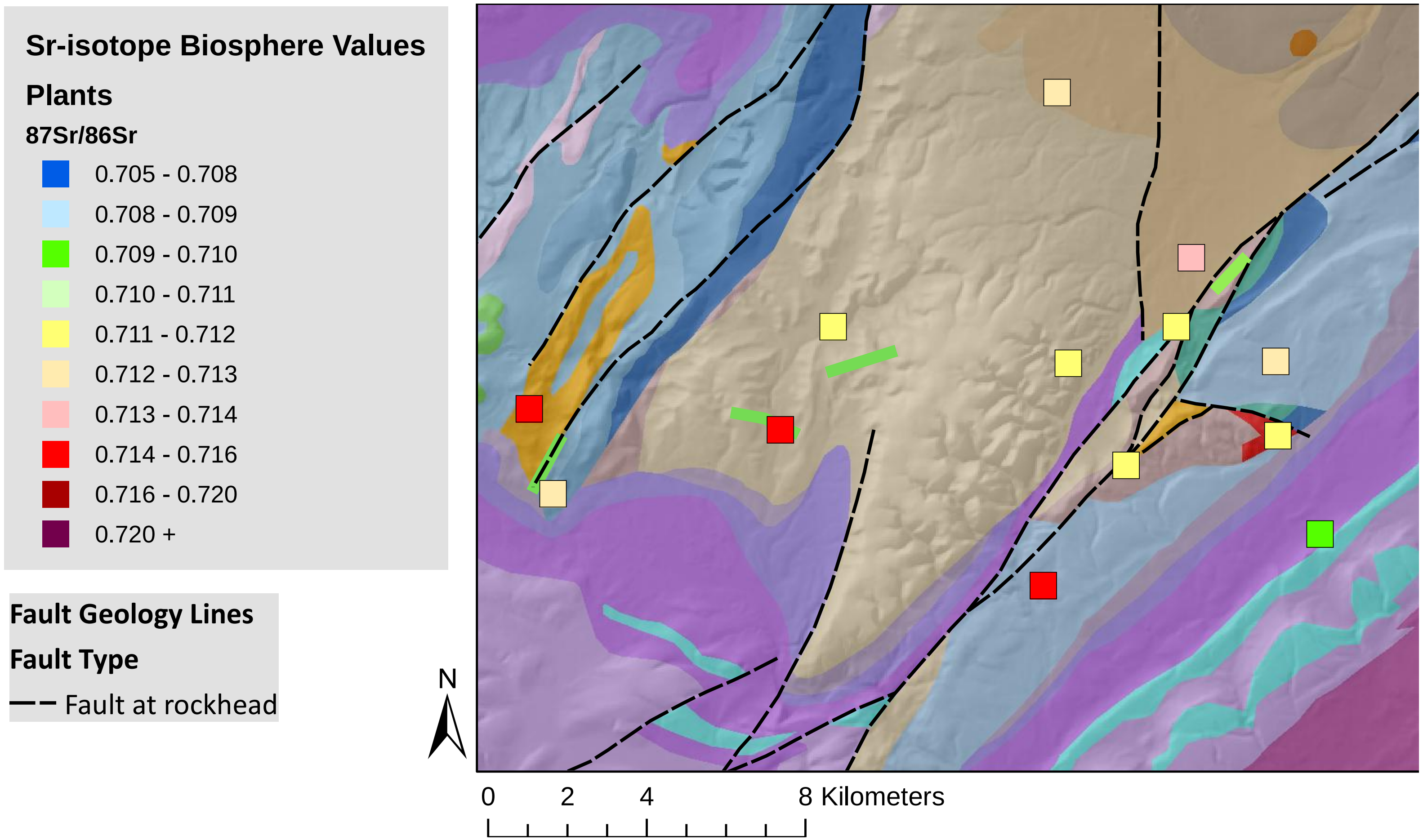


Figure 4.4.1. The plant $^{87}Sr/^{86}Sr$ from across the Church Stretton study area, alongside GIS data of the 1:625000 Bedrock Geology map, including fault lines (BGS, DiGMapGB, 2007). The main legend for the Bedrock geology can be seen in Figure X. The fault lines mainly display the Church Stretton Fault System.

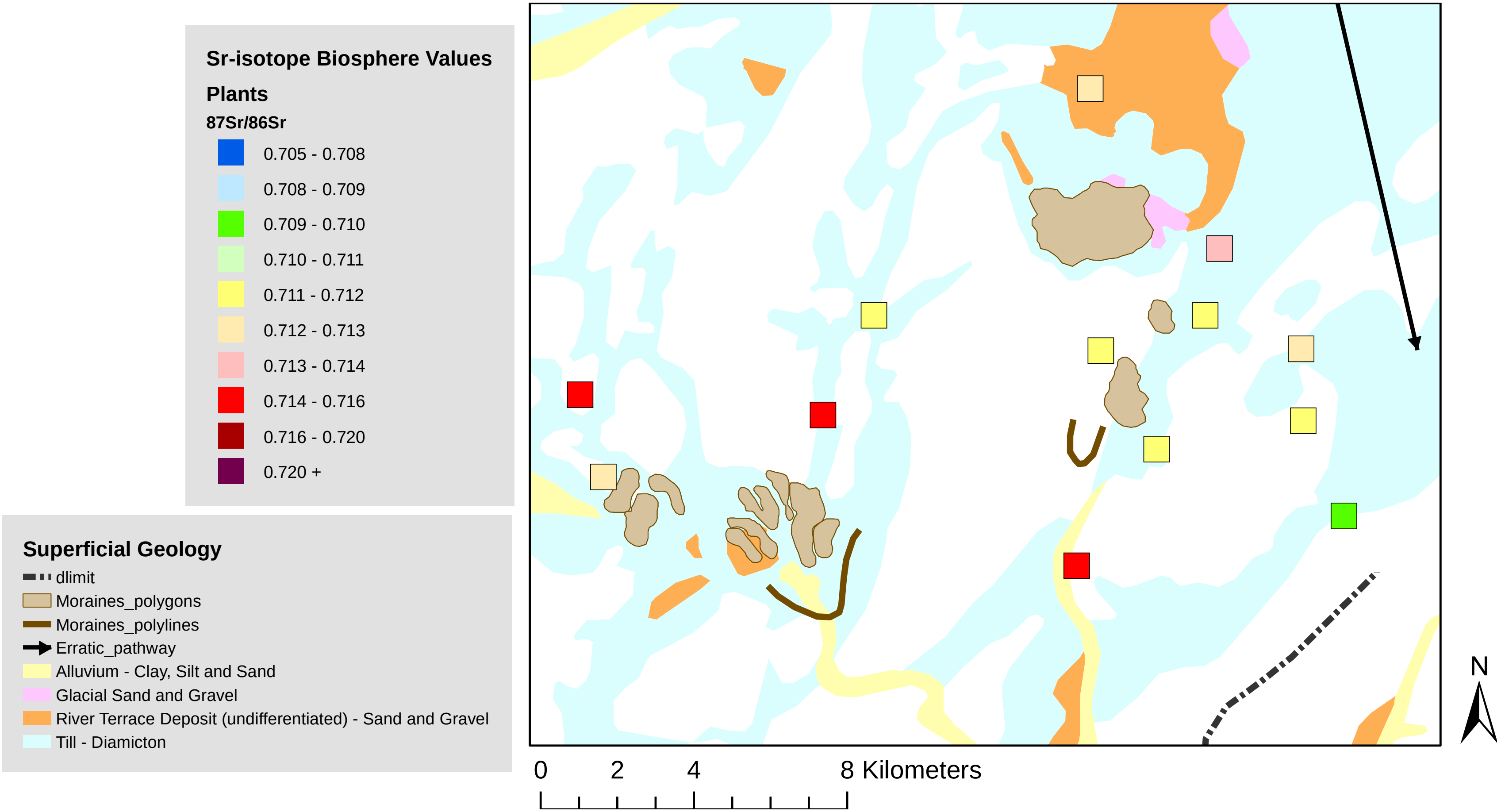


Figure 4.4.2. The plant $^{87}Sr/^{86}Sr$ from across the Church Stretton study area, alongside GIS data of the 1:625000 Superficial Geology map (BGS, DiGMapGB, 1977) and BRITICE (Clark *et al.*, 2004; 2017).

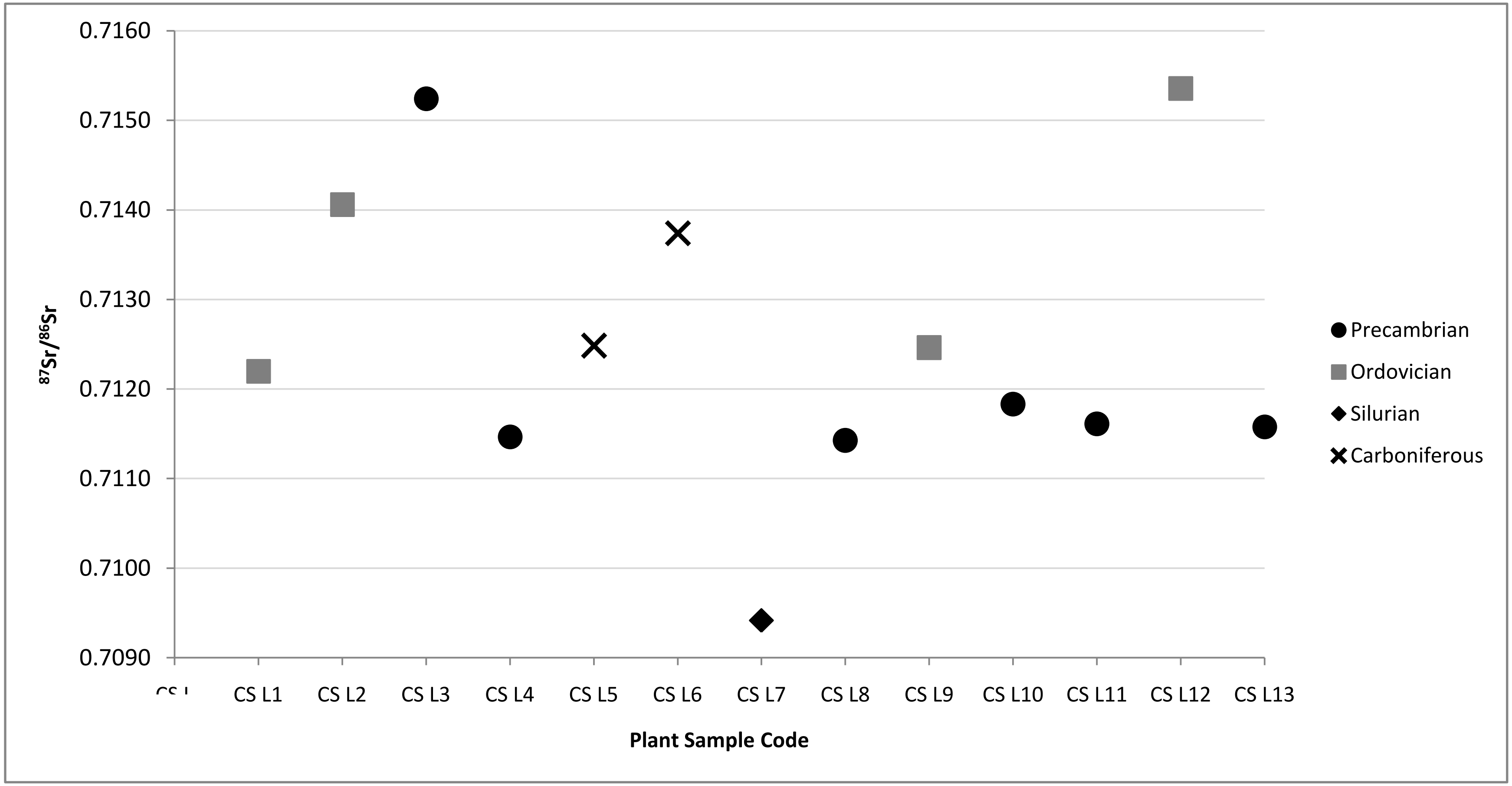


Figure 4.4.3. The plant $^{87}Sr/^{86}Sr$ collected from across the Church Stretton study area, based on the age of the main bedrock geology from which they were taken.

4.5. The Sr-isotope biosphere of the Wrekin, Shropshire, England.

The Wrekin (Figure 1.3 in chapter 1) is a protruding hill in the county of Shropshire (England), approximately 8km west from Telford and 25km north-west of Church Stretton. It formed through faults bringing into contact a variety of bedrock from different ages, notably though the volcanic rocks of the Precambrian Uriconian Group (Pharaoh & Gibbons, 1994). Currently no biosphere $^{87}Sr/^{86}Sr$ data have been recorded within a 35km radius of the area.

The north to north-west Permian bedrock surrounding the Wrekin have an extrapolated $^{87}Sr/^{86}Sr$ package of between 0.709-0.710 according to the preliminary Sr-isotope biosphere map of Britain, while the south and south-east Silurian and Carboniferous bedrocks could produce $^{87}Sr/^{86}Sr$= 0.7117 ±0.0014 (n=10, 1SD, plant samples) and 0.7116 ±0.0003 (n=7, 1SD, water samples) respectively, based on the biosphere $^{87}Sr/^{86}Sr$ data already recorded in Evans *et al.* (2010). Whether the small outcrop of Precambrian Uriconian Group can release radiogenic $^{87}Sr/^{86}Sr$ >0.714 into the biosphere of the Wrekin and immediate area is the main aim of this small study.

4.5.1. Geological Summary of the Wrekin

The bedrock geology of the Wrekin and in the immediate area is very complex, mainly consisting of Precambrian, Cambrian, Carboniferous and Permian lithologies. Figure 4.5.1 displays the bedrock geology of the Wrekin study area, alongside plant $^{87}Sr/^{86}Sr$ data collected in this study. The Precambrian Uriconian Group forms the main ridge of the Wrekin. Its north-western slopes and contains a variety of volcanic lavas (rhyolites mainly) and tuffs, with a granophyric granitic intrusion (Ercallite) to the north-east and several basalt and dolerite dykes cutting through the central to southern parts (BGS, 1978, Sheet 152, Solid; Toghill, 1990, p.12, 24-25). The granophyric granitic intrusion has yielded a concordant U-Pb ziron age of 560 ±1Ma and represents the most reliable maximum age limit yet determined for the Precambrian-Cambrian boundary in southern Britain (in Pharaoh & Gibbons, 1994).

The Cambrian Comley Series, namely the Wrekin Quartzite followed by the Lower Comley Sandstone and Limestones, then unconformably oversteps the Precambrian Uriconian Group on the east to south-eastern side of the hill (BGS, 1978, Sheet 152, Solid; Pharaoh & Gibbons, 1994). Moving eastwards are the Cambrian Merioneth and Tremadoc Series, mainly a succession of shales, which lie unconformably after the Comley Series. These are then overstepped by the Carboniferous Limestone, which also contains the Lydebrook Sandstone and Little Wenlock Basalt, followed unconformably by the Carboniferous Lower and Middle Coal Measures, a large succession of various sedimentary rocks with various coal seams.

On the west to north-western side of the Wrekin, the Precambrian Uriconian Group is bought into contact with the younger Permian Bridgnorth (Lower Mottled) Sandstone via the Wrekin Fault. In turn, moving north-west, the Permian bedrock is bought into contact with the older Carboniferous Keele Beds (purple to brown mudstones and mottles sandstones) of the Upper Coal Measures, via the smaller Cluddley Fault. Then sandwiched between the Burcot and Brockton Faults, the Precambrian Uriconian Group reoccurs, but does not form a protruding hill like the Wrekin and lacks any intrusive igneous rocks. Finally, after the Brockton Fault, the area is once more extensively covered by the Permian Bridgnorth (Lower Mottled) Sandstone (BGS, 1978, Sheet 152, Solid; Toghill, 1990, p.9-16).

The Wrekin is not covered by any Quaternary superficial deposits, but there is extensive glacial till deposits to the north and north-western side (stretching past the village of Cluddley) on the Permian, Carboniferous and Precambrian bedrock described in the previous paragraph above. Some smaller glacial till deposits also lie to the east and south-eastern of the hill, mainly on top of the Carboniferous bedrock (BGS, 1974, Sheet 152, Drift).

4.5.2. Geochemical Survey and Field-notes for the Wrekin

In September 2015 a total of four locations were visited across the Wrekin. The weather over the collection period was sunny and dry. The plant samples were collected and mixed for each location by the methods described in chapter 3, section 3.2. The field-notes for the mixed plant samples from across the Wrekin can be viewed in the Appendix 2. These mixed plant samples then followed the same methods for chemical preparation and Sr-isotope analysis outlined in section 3.3 in chapter 3.

4.5.3. Plant $^{87}Sr/^{86}Sr$ Results and Discussion

The plant $^{87}Sr/^{86}Sr$ from across the Wrekin are displayed in Figure 4.5.1 and 4.5.2. Overall, the average plant $^{87}Sr/^{86}Sr$ = 0.7120 ±0.0011 (n=4, 2SD) for the Wrekin, but if split, the Precambrian Uriconian have plant $^{87}Sr/^{86}Sr$ at 0.71175 (W L4) and 0.71270 (W L2), the Lower Cambrian sedimentary rocks have plant $^{87}Sr/^{86}Sr$ at 0.71203 (W L1) and the Carboniferous Upper Coal Measures have the lowest plant $^{87}Sr/^{86}Sr$ at 0.71134 (W L3).

Over the small study area of the Wrekin there is a west-east trend in the plant $^{87}Sr/^{86}Sr$ (Figure 4.5.1). The lower $^{87}Sr/^{86}Sr$ values ~0.711 are found to the west and the higher ~0.712 to the east. This divide seems to mainly reflect the igneous lithologies of the Precambrian Uriconian Group, which forms the main ridge of the Wrekin. The basalt and dolerite dykes, which are mafic in composition, are more dominant in the central and southern parts of the volcanic outcrop, which is reflected by the plant$^{87}Sr/^{86}Sr$ at 0.71175 (W L4), compared to the northern part, which contains rhyolites and the granophyric granitic intrusion (Ercallite) and produced the highest value at 0.71270 (W L2). Overall though, this northern value on the Precambrian volcanic outcrop is not a radiogenic as expected, considering the felsic composition of the rhyolites and the granophyric granitic intrusion (Ercallite).

The Lower Cambrian sedimentary rocks to the south-east of the Precambrian Uriconian Group, but still on the Wrekin, have plant $^{87}Sr/^{86}Sr$ at 0.71203 (W L1). Considering that there are not any extensive Quaternary superficial deposits covering the Wrekin hill, it is likely that this plant $^{87}Sr/^{86}Sr$ reflects the Cambrian bedrock, which may contain debris eroded from the Precambrian Uriconian Group during its formation and hence have similar $^{87}Sr/^{86}Sr$.

To the north-west of the Wrekin hill, the Carboniferous Upper Coal Measures have plant $^{87}Sr/^{86}Sr$ at 0.71134 (W L3). Even though this area is extensively covered by of glacial till deposits (BGS, 1974, Sheet 152, Drift), it is possible that they contain material from local bedrock and so have not altered the expected biosphere $^{87}Sr/^{86}Sr$. The sample W L3 compares well to other Carboniferous biosphere $^{87}Sr/^{86}Sr$ data, namely the Carboniferous Grits of the Midlands, with water $^{87}Sr/^{86}Sr$ = 0.7116 ±0.0003 (n=7,1SD: Evans *et al.,* 2010) and plant $^{87}Sr/^{86}Sr$ which ranges between 0.71065-0.71283 on the Carboniferous Coal Measures of the Midlands (NIGL, unpublished results) and so raises no concern.

4.5.4. Concluding remarks

Overall, the plant $^{87}Sr/^{86}Sr$ from across the small Wrekin study area have produced no values >0.714. The outcrops of the Precambrian Uriconian Group are possibly too small and varied in igneous composition to produce high values in the biosphere and so any further sampling would only be for the benefit of characterizing the other bedrock geology that surrounds the Wrekin.

Sr-isotope biosphere around the Wrekin (Shropshire, England):

- Overall the Wrekin study area has an average plant $^{87}Sr/^{86}Sr$ = 0.7120 ±0.0011 (n=4, 2SD)
- The Precambrian Uriconian Group plant $^{87}Sr/^{86}Sr$: 0.71175 (W L4) and 0.71270 (W L2)
- The Lower Cambrian sedimentary rocks plant $^{87}Sr/^{86}Sr$: 0.71203 (W L1)
- The Carboniferous Upper Coal Measures plant $^{87}Sr/^{86}Sr$: 0.71134 (W L3)

4.5.Figures

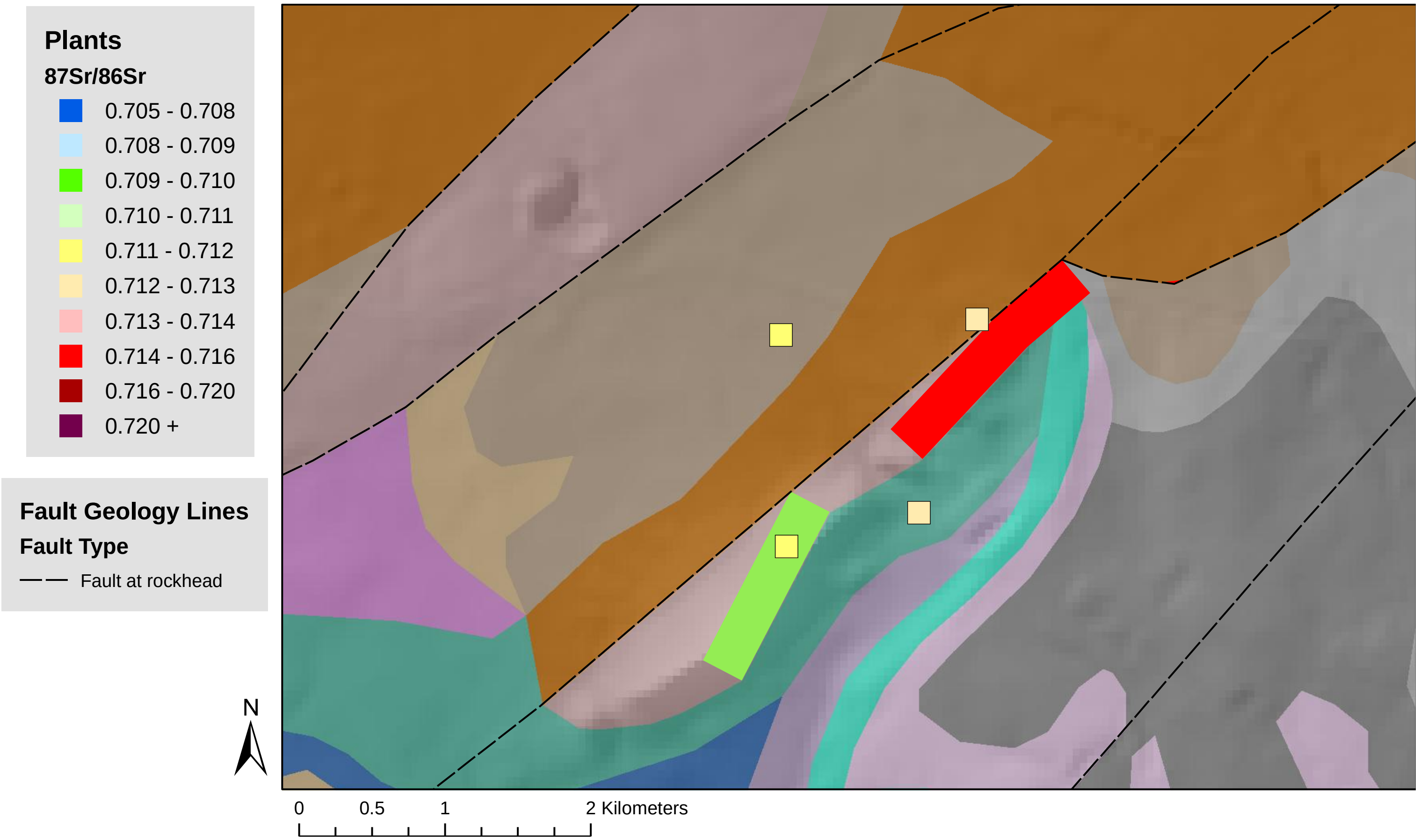


Figure 4.5.1 The plant $^{87}Sr/^{86}Sr$ from across the Wrekin study area, alongside GIS data of the 1:625000 Bedrock Geology map, including fault lines (BGS, DiGMapGB, 2007). The main legend for the Bedrock geology can be seen in Figure X. The central fault is the Wrekin Fault, then heading northwards are the Burcot and Brockton Faults respectively. The fault to the south/south-east is the Lightmoor Fault (based on the BGS 1:50000 Solid Geology map, 1978, Sheet 152).

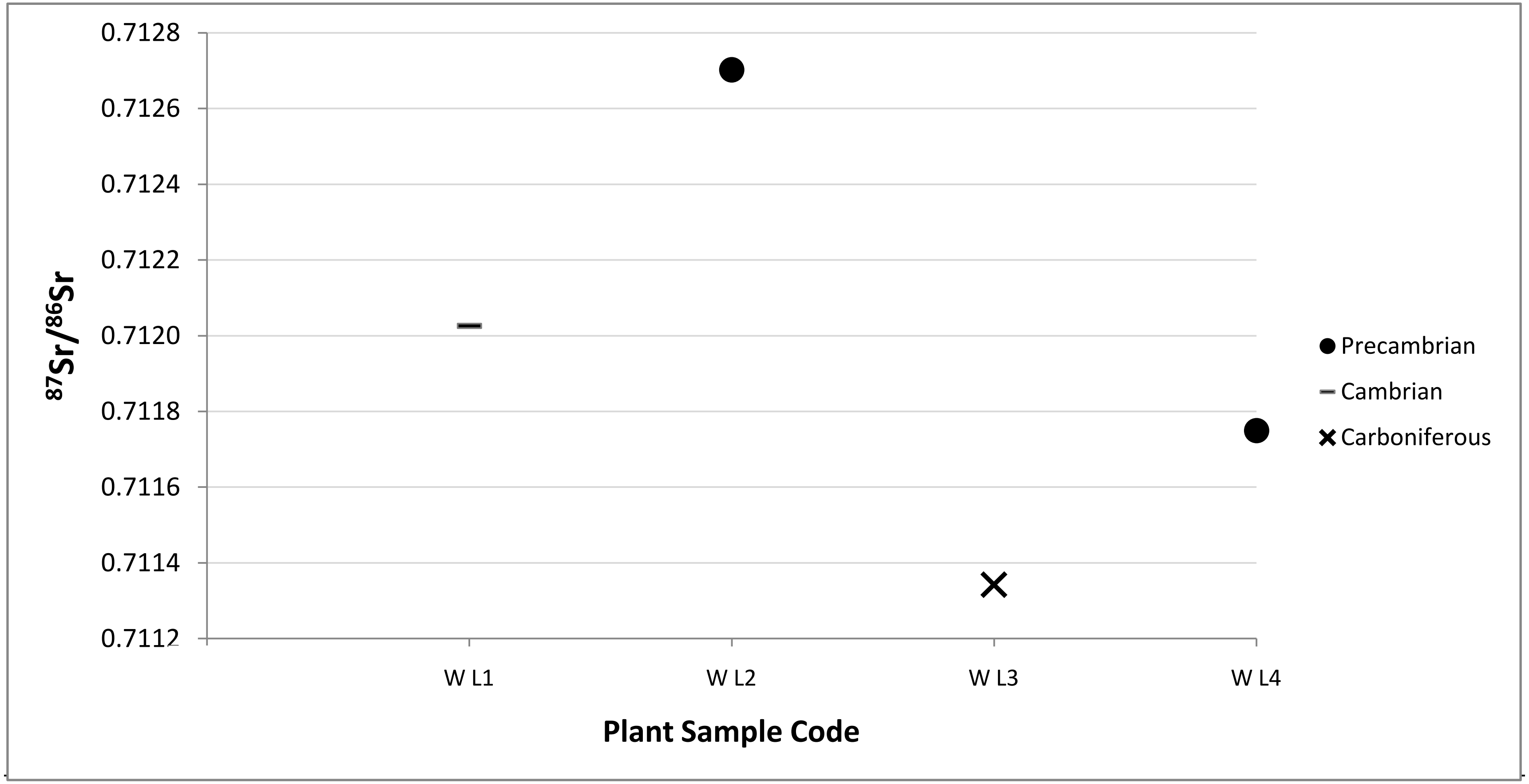


Figure 4.5.2. The plant $^{87}Sr/^{86}Sr$ collected from across the Wrekin study area, based on the age of the main bedrock geology from which they were taken.

4.6. The Sr-isotope biosphere surrounding Kington, Herefordshire, England: The Stanner-Hanter Complex

To the south of the Welsh Borderlands Fault System, between the market town of Kington, Herefordshire (England: Figure 1.3 in chapter 1) and New Radnor, Powys (Wales) are exposures of Precambrian bedrock, with two small fault-bound lenses of altered igneous intrusions known as the Stanner-Hanter Complex (Pharaoh & Gibbons, 1994). The complex forms the Stanner Hill and Hanter Hill. No biosphere $^{87}Sr/^{86}Sr$ data have been recorded on the Stanner-Hanter Complex, but approximately 15km north-east, around Knighton (Powys, Wales), a water sample taken from Silurian bedrock has a $^{87}Sr/^{86}Sr$ at 0.71393 (JMW 05: Montgomery *et al.,* 2006), while to the south-west, near to the village of Erwood (Powys, Wales), the Silurian bedrock has recorded plant $^{87}Sr/^{86}Sr$ at 0.71012, 0.71230, 0.71334 and 0.71550 (USK-01 to -04: Evans, *pers.com*.).

4.6.1. Geological Summary of the Stanner-Hanter Complex and surrounding area

The bedrock geology in the Kington study area can be seen in Figure 4.6.1, alongside the plant $^{87}Sr/^{86}Sr$ data. The Stanner-Hanter Complex currently records the oldest isotopic ages of any Precambrian igneous rocks in southern Britain, with the granitic rocks within the complex giving a Rb-Sr isochron age of 702 ±8Ma (in Pharaoh & Gibbons, 1994) and a U-Pb zircon age of 710.8 ±1.5Ma (Schofield *et al.,* 2010). Although this complex is similar to the Uriconian Group, found approximately 50km north-east around the town of Church Stretton and the Wrekin (Shropshire, England), it is significantly older and so is considered separate and distinct assemblage of intrusive rocks (Schofield *et al.,* 2010). The complex mainly contains highly altered dolerite and gabbro, and smaller felsic components like granophyric granite (Pharaoh & Gibbons, 1994; BGS, 2004, Sheet 197; Schofield *et al.,* 2010).

Just to the north-west of the Stanner-Hanter Complex, around Old Radnor (Powys, Wales), is a Precambrian inlier of the Longmyndian, mainly the Strinds Formation, consisting of micaceous green-grey sandstones and the Yats Wood Formation, varying green-grey mud-, silt- and sandstones (Woodcock & Pauley, 1989; BGS, 2004, Sheet 197). The Longmyndian lithologies are overlain unconformably by the Silurian (Wenlock) Dolyhir Limestone Formation to the west (Woodcock & Pauley, 1989; BGS, 2004, Sheet 197), while both the remaining sides of Longmyndian are bought into fault contact with the Silurian Wenlock and Ludlow undifferentiated mud-, silt- and sandstones (Woodcock & Pauley, 1989; BGS, 2004, Sheet 197). The Stanner-Hanter complex is overstepped by the same undifferentiated Silurian strata above to the southern and eastern margins and faulted along the north (BGS, 2004, Sheet 197; Schofield *et al.,* 2010).

The Quaternary superficial deposits are not mapped on the BGS 1:625 000 Superficial Geology map, but are present on the BGS 1:50 000 Bedrock and Superficial Geology map (2004, Sheet 197). The Stanner-Hanter Complex and the Longmyndian lithologies around Old Radnor are not covered by any extensive superficial deposits. Instead till deposits are mainly found to the north-west of the Precambrian inliers while between them lie a mix of mainly glaciofluvial sheet deposits and alluvium. Some head deposits can be found upon the west side of the Longmyndian lithologies and the Silurian Dolyhir Limestone Formation (BGS, 2004, Sheet 197).

4.6.2. Geochemical Survey and Field-notes for the Stanner-Hanter Complex

In September 2015 a total of 5 locations were visited between the market town of Kington (Herefordshire, England) and the village of New Radnor (Powys, Wales). The weather over the collection period was mainly cloudy but with no rain. The plant samples were collected and mixed for each location by the methods described in chapter 3, section 3.2. The field-notes for the mixed plant samples from across the 5 locations can be viewed in the Appendix 2. These mixed plant samples then followed the same methods for chemical preparation and Sr-isotope analysis outlined in section 3.3 in chapter 3.

4.6.3. Plant $^{87}Sr/^{86}Sr$ Results and Discussion

The plant $^{87}Sr/^{86}Sr$ results from around the Stanner-Hanter Complex are displayed in Figure 4.6.1 and 4.6.2. The Silurian sedimentary rocks have recorded the highest plant sample, SHC L5, with a $^{87}Sr/^{86}Sr$ at 0.71613. This sample was collected from woodland (Appendix 2). The other plant $^{87}Sr/^{86}Sr$ on the Silurian sedimentary rocks in the Kington study area, not taken from woodland, has a value of 0.71314 (SHC L1), which is a difference of approximately +0.003 between the two samples. SHC L5 compares well with another plant sample also collected from woodland on the same Silurian bedrock, USK-04 with a $^{87}Sr/^{86}Sr$ at 0.71550 (Evans, pers.com.). The previously proposed woodland effect (chapter 2, section 2.4.3) may be the cause of these high values and thus the data from the Stanner-Hanter Complex contributes further evidence that this is a significant but previously unobserved phenomenon.

The Precambrian bedrock, including the highly altered dolerite and gabbro of the Stanner-Hanter Complex and the Longmyndian sedimentary rocks, has a plant $^{87}Sr/^{86}Sr$ = 0.7123 ±0.001 (n=3, 2SD). Both the highest and the lowest plant $^{87}Sr/^{86}Sr$ are on the Stanner-Hanter Complex, at 0.71192 (SHC L2) and 0.71270 (SHC L3), respectively. The lowest value (SHC L2) is located at the base of Hanter Hill (and therefore part of the Stanner-Hanter Complex) where Quaternary glaciofluvial and more modern alluvial fan deposits were present. These quaternary superficial deposits could easily contain material from the nearby Dolyhir Limestone Formation (dating to the Silurian: BGS, 2004, Bedrock & Superficial Geology, Sheet 197), which is likely to be preferentially weathered over the lithologies of the Precambrian inliers. That said, the difference of approximately +0.0008 between the two samples on the Stanner-Hanter Complex could just as easily be explained by the heterogeneous nature of its dolerite and gabbro rocks.

The sample SCH L4, with $^{87}Sr/^{86}Sr$ at 0.71220, located on the Precambrian Longmyndian, is only slightly higher than the plant $^{87}Sr/^{86}Sr$= 0.7116 ±0.0003 (n=5, 2SD) on the Precambrian Uriconian and the Longmyndian lithologies in the Church Stretton study area (section 4.4.3). Currently, there is no clear distinction between the plant $^{87}Sr/^{86}Sr$ on the Stanner-Hanter Complex or the Longmyndian sedimentary rocks in the Kington study area, but together they stand out as less radiogenic than the surrounding Silurian sedimentary bedrock.

4.6.4. Concluding remarks

Only one out of the five mixed plant samples collected recorded a $^{87}Sr/^{86}Sr$ value >0.714: SHC L5 at 0.71613. This sample was not located on the Precambrian inliers of the Stanner-Hanter Complex or Longmyndian, but on the Silurian bedrock. It was also taken from woodland and may be elevated due to the woodland effect. Considering the small size of the Precambrian inliers, it is unlikely that further sampling from the Precambrian bedrock will produce a high biosphere, i.e. $^{87}Sr/^{86}Sr$ >0.714. However, the Silurian sedimentary bedrock has produced some notable values that require further consideration.

Sr-isotope biosphere around Kington (Herefordshire, England):

- Precambrian inliers (the Stanner-Hanter Complex and the Longmyndian) plant $^{87}Sr/^{86}Sr$: 0.7123 ±0.001 (n=3, 2SD)
- Silurian sedimentary bedrock plant $^{87}Sr/^{86}Sr$: 0.71314 (SHC L1) and 0.71613 (SHC L5)

4.6. Figures

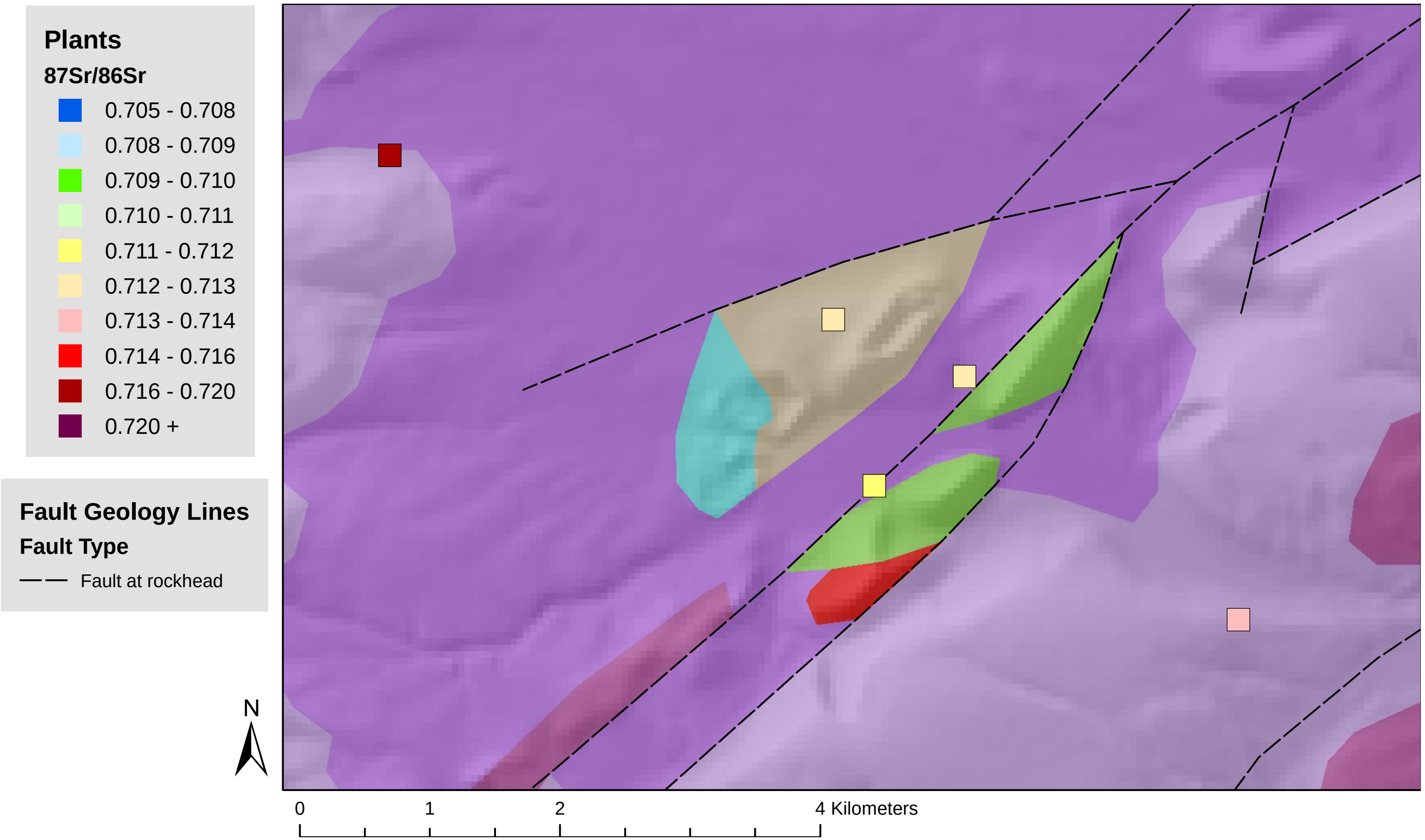


Figure 4.6.1. The plant $^{87}Sr/^{86}Sr$ from across the Kington study area, alongside GIS data of the 1:625000 Bedrock Geology map, including fault lines (BGS, DiGMapGB, 2007). The main legend for the Bedrock geology can be seen in Figure X.

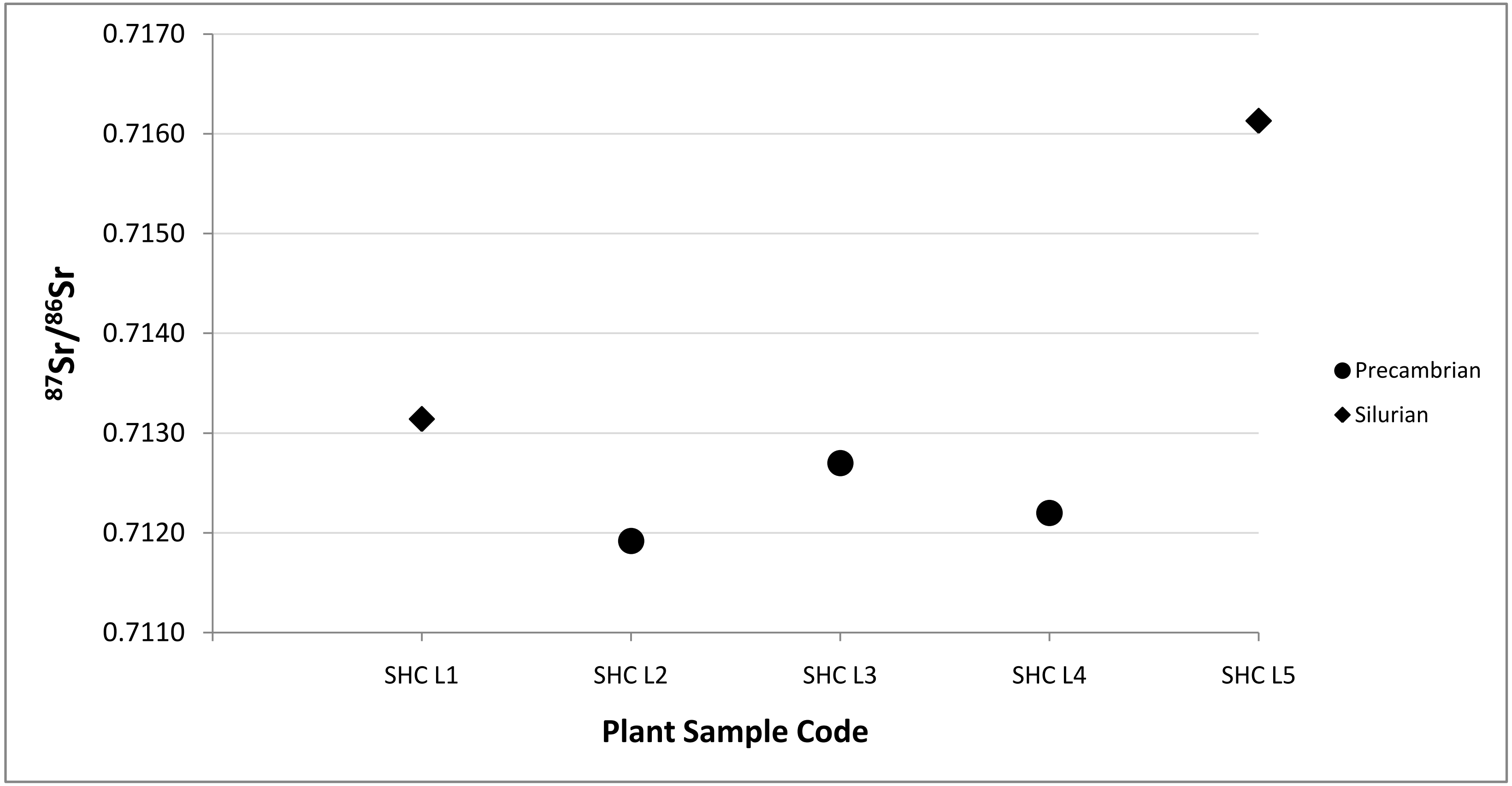


Figure 4.6.2. The plant $^{87}Sr/^{86}Sr$ collected from across the Kington study area, based on the age of the main bedrock geology from which they were taken.

4.7. The Sr-isotope biosphere of the Lake District, Cumbria, England.

The Lake District (Figure 1.3 in chapter 1) is a region and national park found in the north-east of England, in the county of Cumbria. It is renowned for its scenic glacial lakes and rugged mountains. These mountains first formed through a complex geological history, starting in the early Ordovician with the sedimentary rocks of the Skiddaw Group, followed by the formation of the Borrowdale Volcanic Group. Underpinning these groups is a large granitic batholith that formed in the late Ordovician, exposed in the western parts of the Lake District as the Eskdale and Ennerdale intrusions. The southern part of the Lake District mainly consists of sedimentary rocks of the Windermere Supergroup, which dates to the Silurian, while surrounding the Lake District are a variety of sedimentary bedrocks dating from the Carboniferous to the Triassic. Finally, the Lake District has been further shaped and modified, along with the formation of the glacial lakes, during repeated glaciations of the Quaternary (Millward *et al.,* 2000). A more detailed geological summary of the Lake District can be seen below in section 4.7.1.

Only a couple of biosphere $^{87}Sr/^{86}Sr$ values are currently available from the Lake District and they are both coastal. One mineral water sample is to the south, near Grange-over-Sands (Morecambe Bay, Cumbria), with $^{87}Sr/^{86}Sr$ at 0.70959 (JMW 16: Montgomery *et al.,* 2006), the other is to the west, around the village of St Bees (Copeland, Cumbria), with a dentine $^{87}Sr/^{86}Sr$ at 0.7094 (Bees-10bd: Knüsel *et al.,* 2010). Both are based on the Triassic Sherwood Sandstone Group. As both these samples were excavated at coastal sites they are likely to be influenced by marine Sr (~0.7092: Veizer, 1989, p.142), but they fall into the expected range of biosphere values displayed from Triassic bedrock, with water $^{87}Sr/^{86}Sr$ = 0.7097 ±0.0006 (n=29, 1SD: Evans *et al.,* 2010).

To the north-east, approximately 10km north of Penrith, there is another mineral water sample from Permian sedimentary bedrock with $^{87}Sr/^{86}Sr$ at 0.71005 (JMW 15: Montgomery *et al.,* 2006). Being >40km away from the coast this value is thought to be reflective of the Permian bedrock geology.

The mean annual rainfall of the Lake District exceeds 1250mm, with the central parts receiving over 3000mm (Met Office, Rainfall amount Annual Average, 1981-2010). It is possible therefore that the Sr-isotope biosphere of the Lake District will be heavily influenced by atmospheric Sr (~0.7092: Veizer, 1989, p.142), but the large granitic intrusions, as well as the Borrowdale Volcanic Group, dating to the Ordovician make the Lake District a potential area within England that could produce $^{87}Sr/^{86}Sr$ >0.714.

4.7.1. Geological Summary of the Lake District

The bedrock geology of the Lake District study area can be seen in Figure 4.7.1, alongside the plant $^{87}Sr/^{86}Sr$ data. A simplified geological map of the Lake District can also be viewed in Figure 4.7.2 (taken from Figure 1 in Millward *et al.,* 2000, p.ii). The Lake District lies within a Lower Palaeozoic inlier, consisting of strata dating from the Ordovician through to the Devonian (best displayed in Figure 4.7.2). Younger strata from the Carboniferous to the Triassic, which surround the Lake District inlier, were eroded during the Lake District's complex geological history, before being overlain by Quaternary superficial deposits. The Lake District has a complex fault pattern as well as extensive folding (e.g. the Scafell and Ulpha synclines are well known to geologists), these are most predominant in the Borrowdale Volcanic Group and the Eskdale Pluton (Millward *et al*., 2000, p.6-7). The bedrock geology of the Lake District is complex and descriptions of the stratigraphy, etc., is thus summarised below .

4.7.1.1. The Cambro-Ordovician

The oldest lithologies in the Lake District belong to the Skiddaw Group. This group is mainly found in the northern part of the district, as well as at the Black Combe fell to the south-west of the district near the coast (Figure 4.7.2: BGS, 1998, Sheet 38; BGS, 1999, Sheet 29; Millward *et al.*, 2000, p.1-2). The group mainly comprises turbiditic sand-, silt- and mudstones deposited in a marine environment, at the continental margin of microcontinental terrane called Avalonia during the late Cambrian to early Ordovician. The Skiddaw Group is the original substrate to the volcanoes that formed during the later Ordovician (Millward *et al.,* 2000, p.1-2,7-8).

4.7.1.2. The Ordovician to Silurian

The Borrowdale Volcanic Group, which dominates the central part of the district (Figures 4.7.1 and 4.7.2), consists of the remnants of the volcanoes that formed and erupted during the Ordovician. This group forms an 8km-thick succession that can be split into two distinctive volcanic episodes. The first episode was dominated by eruptions of andesite and basalt lavas (the Birker Fell Formation) and the second dominated by explosive volcanism and caldera formation resulting in mainly pyroclastic rocks, such as tuffs and ignimbrites, intercalated with volcaniclastic sedimentary rocks. The composition of the explosive episode can change from andesitic, to dacitic to rhyolitic. The volcanism represents the subduction zone that formed during the closure and destruction of the Iapetus Ocean, as plate tectonics cause the collision of the continents of Laurentia in the north to Avalonia-Gondwana in the south (BGS, 1998, Sheet 38; Millward *et al.,* 2000, p.2-3, 7).

The Windermere Supergroup is found in the southern part of the district and lies unconformably above the Borrowdale Volcanic Group (Figure 4.7.2). The Supergroup dates from the late Ordovician to the Silurian, when magmatism waned and subsidence increased, which resulted in the formation of a basin in the final stages of Iapetus Ocean closure. The lithologies comprise of a sequence of folded and cleaved marine sedimentary rocks. At the base of the Supergroup is the Dent Group, which dates to the late Ordovician and comprises of limestone, calcareous sandstone and siltstone, with pockets of conglomerate and thin beds of acidic tuffs near the top of the group. Deposition was continuous into the Silurian with a succession of largely graptolite-bearing hemipelagite of the Stockdale Group, which progressively became more turbiditic with deposition of mud-, silt and sandstones throughout the Wenlock and Ludlow of the Silurian Period (BGS, 1998, Sheet 38; Millward *et al.,* 2000, p.3-4, 8).

4.7.1.3. The Ordovician to Devonian Igneous Intrusions

The Lake District is underpinned by an Ordovician to Devonian granitic batholith, which is exposed in the westernmost part as the Eskdale and Ennerdale intrusions (Figure 4.7.1 and 4.7.2). The Eskdale intrusion, commonly called the Eskdale Pluton, comprises of the Eskdale granite and the Eskdale granodiorite, both of which are considered to be coeval (Millward *et al.,* 2000, p.4). The Eskdale granite, found in the northern part of the pluton, consists of three main varieties: the medium-grained aphyric (lack of phenocrysts) muscovite granite, known as the ‘normal' granite; a series of microgranites; and a coarse- to very coarse-grained granite (Young, 1999; Millward *et al.,* 2000, p.4). Whole-rock $^{87}Sr/^{86}Sr$ values between 0.72436 - 1.11430 (n=10), with a mean of 0.95715, are recorded from the Eskdale granite by Rundle (1979), which means the granite has the potential to release high $^{87}Sr/^{86}Sr$ into the biosphere. The Eskdale granodiorite, found in the southern part of the pluton, is described as being medium grained and richer in the feldspar mineral plagioclase and the mica mineral biotite while poorer in the mica mineral muscovite compared to the Eskdale granite (Millward *et al.,* 2000, p.4). Whole-rock $^{87}Sr/^{86}Sr$ = 0.71734 - 0.92781 (n=12) for the granodiorite (Rundle, 1979), with a mean value of 0.74111, which is still a high value, but less so than the granite.

The Ennerdale intrusion, commonly known as the Ennerdale Granophyre, is to north of the Eskdale Pluton. It forms three outcrops, which cover approximately 16km^2, with the main lithology being a leucocratic, fine-grained, slightly porphyritic granite, commonly with a granophyric texture. Diorites also occur locally adjacent to the margins of the intrusion. The Ennerdale Granophyre have whole-rock $^{87}Sr/^{86}Sr$ between 0.71280 - 0.80063 (n=10), with a mean of 0.75333 (Rundle, 1979), overall being more similar to the Eskdale granodiorite described above. There are also several minor intrusions (Figure 4.7.1), ranging in age from Ordovician to Devonian and comprise of mainly aphyric basalt, dolerite, and rhyolite dykes. These dykes are abundant within the Skidaw Group, Borrowdale Volcanic Group and around the margins of the Eskdale Pluton. Some also intruded into the Eskdale Pluton and some are present within the Windermere Supergroup, but not as abundant as in the above groups (Millward *et al.,* 2000, p.5).

4.7.1.4. The Carboniferous to Triassic

Surrounding the Lake District Lower Palaeozoic inlier are a variety of sedimentary lithologies dating from the Carboniferous to the Triassic (Figure 4.7.1). The Carboniferous rocks surround all but the western side of the Lake District inlier. They largely consist of limestone with subordinate mud-, silt- and sandstone from the Yordale Group (BGS, 1997, Sheet 23; BGS, 2004, Sheet 30), while to the north-west of the district are mud-, silt- and sandstones, with numerous coal seams, of the Pennine Coal Measures, along with reddened silt- and sandstones of the Warwickshire Group (BGS, 2004, Sheet 28). To the north-east, overstepping the Carboniferous bedrock are red sandstones with breccia (sometimes containing clasts of limestone from the Carboniferous) of the Appleby Group and mud-, silt- and sandstones with some thin limestone and evaporite beds of the Cumbrian Coast Group, which date to the Permian (BGS, 2004, Sheet 30).

The Triassic rocks found to the west of the Lake District, along the coast, mainly belong to the Sherwood Sandstone Group, which is a large succession of red, brown and yellow sandstones with some subordinate siltstones (BGS, 1999, Sheet 37).

4.7.1.5. The Quaternary Superficial Deposits

Repeated glaciations during the Quaternary have modified the topography of the Lake District and surrounding area, as well as leaving behind extensive superficial deposits (Figure 4.7.3). The most common Quaternary deposit is glacial till from the late Devensian glaciation (BGS, 1998, Sheet 38; BGS, 1999, Sheet 29; Millard *et al.,* 2000, p.5), which tends to thin to the west (<5m thick) compared to the east of the district which averages >10m thick). In the south, over the Windermere Supergroup, the till has been extensively shaped into drumlins (Millward *et al.,* 2000, p.5). Other glacial deposits, such as moraine deposits (marking the retreat of the glaciers) and glaciofluvial deposits to the west and south-west of the district, are also common.

There are many postglacial deposits scattered across the district, with alluvium underlying present-day floodplains and alluvial fan deposits occurring notably in Wasdale, Eskdale, the Duddon Valley and Great Langdale. Peat deposits (up to 3m thick) are more common to the west, just south of the Eskdale Pluton, while scree and head deposits are widespread across the whole district (BGS, 1998, Sheet 38; BGS, 1999, Sheet 29; Millard *et al.,* 2000, p.5).

4.7.2. Geochemical Survey and Field-notes for the Lake District

In January 2015 one location was visited (LD L17) on the Eskdale Pluton and in July 2015 a further 16 locations were visited across the whole Lake District study area. The weather over the collection period in January was wet with heavy showers, while in July it was mainly sunny with brief periods of light rain. The plant samples were collected and mixed for each location by the methods described in chapter 3, section 3.2. The field-notes for the mixed plant samples from across the Lake District can be viewed in the Appendix 2. These mixed plant samples then followed the same methods for chemical preparation and Sr-isotope analysis outlined in section 3.3 in chapter 3.

4.7.3. Plant $^{87}Sr/^{86}Sr$ Results and Discussion

The plant $^{87}Sr/^{86}Sr$ results collected from across the Lake District study area can be seen in Figure 4.7.1, 4.7.3 and 4.7.4. The sedimentary rocks of the Skiddaw Group have plant $^{87}Sr/^{86}Sr$ = 0.7106 ±0.0019 (n=5, 2SD) and the Ordovician lavas, tuffs and volcaniclastic rocks of the Borrowdale Volcanic Group have plant $^{87}Sr/^{86}Sr$ = 0.7102 ±0.0021 (n=6, 2SD). The mixed plant samples LD L12 and LD L14, on the Borrowdale Volcanic Group and Skiddaw Group respectively, have $^{87}Sr/^{86}Sr$ values which are different by +0.001 compared to all the other samples collected from both bedrocks (Figure 4.7.4). According to the field-notes (Appendix 2) the locations and plants collected were not unusual. The only similarities are that they have are that they are both on post-glacial alluvium, near lakes and taken from woodlands.

As alluvium is deposited by a river, it could be that the superficial deposits contain sediments from upstream that are more radiogenic and so have influenced the plant $^{87}Sr/^{86}Sr$. Any Sr input from the lake water may be very similar to the alluvium above. The lake water will have $^{87}Sr/^{86}Sr$ that reflects a combination of rainwater, the river feeder systems and equilibration with the lake bed (Evans *et al.,* 2010), with the latter two being more influential if higher values >0.712 are to be produced. The woodland effect (chapter 2, section 2.4.3) has also been observed in previous studies in this thesis and could also explain why these values are higher.

If LD L12 and LD L14 are excluded, the precision of the mean plant $^{87}Sr/^{86}Sr$ on these bedrocks increases to 0.7102 ±0.0007 (n=4, 2SD) for the Skiddaw Group and 0.7098 ±0.0007 (n=5, 2SD) for the Borrowdale Volcanic Group. Albeit it is a slightly more elevated mean average, there is still no clear distinction between the plants on the Skiddaw Group and the Borrowdale Volcanic Group, as $^{87}Sr/^{86}Sr$ values can fall within two standard deviations of each other. The plant $^{87}Sr/^{86}Sr$ from both these groups compare well to other plant $^{87}Sr/^{86}Sr$= 0.7105 ±0.0008 (n=11, 1SD) obtained from Ordovician sedimentary bedrock in Wales (Evans *et al.,* 2010).

The plant $^{87}Sr/^{86}Sr$ on the Eskdale granites of the Eskdale Pluton have values of 0.71053 (LD L9), 0.71298 (LD L17) and 0.71471 (LD L8). The latter two values are the highest seen in the Lake District. Considering the whole-rock $^{87}Sr/^{86}Sr$ = 0.72436 - 1.11430 (n=10: Rundle, 1979) for the Eskdale granite though, the plant $^{87}Sr/^{86}Sr$ values are a lot lower on this bedrock. The highest, LD L8, comes from Beckfoot quarry, where the soil was thin and the plants were directly rooted in the exposed rock. The $^{87}Sr/^{86}Sr$ value most likely represents the plants access to bioavailable Sr from the mineral decomposition of the rock they are rooted in, resulting in a higher value. This value has been produced by unusual circumstances and is likely to represent the highest value that may be expected from granitic bedrock. It should not be seen as a typical plant value though, instead the sample LD L17, with $^{87}Sr/^{86}Sr$ at 0.71298, over 1km to the west, is considered a better representation of the biosphere $^{87}Sr/^{86}Sr$ on the granitic bedrock. The lowest plant value on the Eskdale granite, at 0.71053 (LD L10) was collected from heath land, at an elevation of 389m above sea level (the highest location collected from in the district) and potentially represents atmospheric Sr (~0.7092: Veizer, 1989, p.142) saturating the biosphere, leading to a lower value than expected on this bedrock.

The Silurian sedimentary rocks of the Windermere Supergroup, have plant $^{87}Sr/^{86}Sr$ at 0.71185 (LD L15). This value compares well to other biosphere $^{87}Sr/^{86}Sr$ taken from Silurian bedrock, with plant $^{87}Sr/^{86}Sr$ = 0.7117 ±0.014 (n=10, 1SD: Evans *et al.,* 2010). More sampling would be needed to characterize the biosphere $^{87}Sr/^{86}Sr$ on the Windermere Supergroup if needed for any migration or mobility studies, as LD L15 is the only sample on this bedrock in the Lake District currently.

All the plant $^{87}Sr/^{86}Sr$ near the coast follow the same observations made in Bentley (2006, p.152-153) and Montgomery, (2010), where marine sea-spray and atmospheric Sr (~0.7092: Veizer, 1989, p.142) dominate the $^{87}Sr/^{86}Sr$ in the biosphere. Within 10km of the coast, plant $^{87}Sr/^{86}Sr$ = 0.7096 ±0.0007 (n=6, 2SD), not including the samples from the Eskdale granite (LD L8 and LD L17). These coastal samples cover a variety of bedrocks, with some having $^{87}Sr/^{86}Sr$ notably different values from expected. For example, the Carboniferous Coal Measures have a plant $^{87}Sr/^{86}Sr$ of 0.70968 (LD L2) in this study, while in comparison water $^{87}Sr/^{86}Sr$ = 0.7116 ±0.0003 (n=7, 1SD) and 0.7126 ±0.0001 (n=4, 1SD) on the Carboniferous Grits of the Midlands and South Devon respectively, as reported by Evans *et al.* (2010). Also the Coal Measures in the Forest of Dean have plant $^{87}Sr/^{86}Sr$ = 0.71218 ±0.00107 (n=4, 2SD: Chenery *et al.*, 2010; chapter 7, section 7.6.1). The sample LD L2 has a difference of approximately -0.002 to -0.003 compared to these other Carboniferous biosphere values. Instead its $^{87}Sr/^{86}Sr$ is more similar to marine and atmospheric $^{87}Sr/^{86}Sr$ at 0.7092 (Veizer, 1989, p.142). Sea-spray and atmospheric Sr were expected to be major contributors to the biosphere $^{87}Sr/^{86}Sr$ near the coast, considering mean average rainfall >1250mm is experienced annually in the Lake District (Met Office, Rainfall amount Annual Average, 1981-2010).

4.7.4. Concluding remarks

Only one plant sample has $^{87}Sr/^{86}Sr$ >0.714 in the Lake District . However, this sample, LD L8 with a value of 0.71471, is rooted into the Eskdale granite at Beckfoot quarry and so is considered to represent the maximum biosphere $^{87}Sr/^{86}Sr$ available from this bedrock. As a consequence, it should not be seen as a typical plant value on the Eskdale granite. All other plant $^{87}Sr/^{86}Sr$ are <0.714 in the Lake District and all the samples within 10km the coast, excluding those on the Eskdale granite, have plant $^{87}Sr/^{86}Sr$ = 0.7096 ±0.0007 (n=6, 2SD), regardless of the underlying bedrock geology.

Sr-isotope biosphere of the Lake District (Cumbria, England):

- The Cambro-Ordovician Skiddaw Group plant $^{87}Sr/^{86}Sr$ = 0.7102 ±0.0007 (n=4, 2SD), with one elevated value at 0.71227 (LD L14)
- The Ordovician Borrowdale Volcanic Group plant $^{87}Sr/^{86}Sr$= 0.7098 ±0.0007 (n=5, 2SD), with one elevated value at 0.71221 (LD L12)
- The Ordovician Eskdale granite of the Eskdale Pluton plant $^{87}Sr/^{86}Sr$: 0.71053 (LD L9), 0.71298 (LD L17) and 0.71471 (LD L8)
- The Silurian Windermere Supergroup plant $^{87}Sr/^{86}Sr$: 0.71185 (LD L15).
- Within 10km of coast, excluding those on the Eskdale granite, plant $^{87}Sr/^{86}Sr$ = 0.7096 ±0.0007 (n=6, 2SD).

4.7. Figures

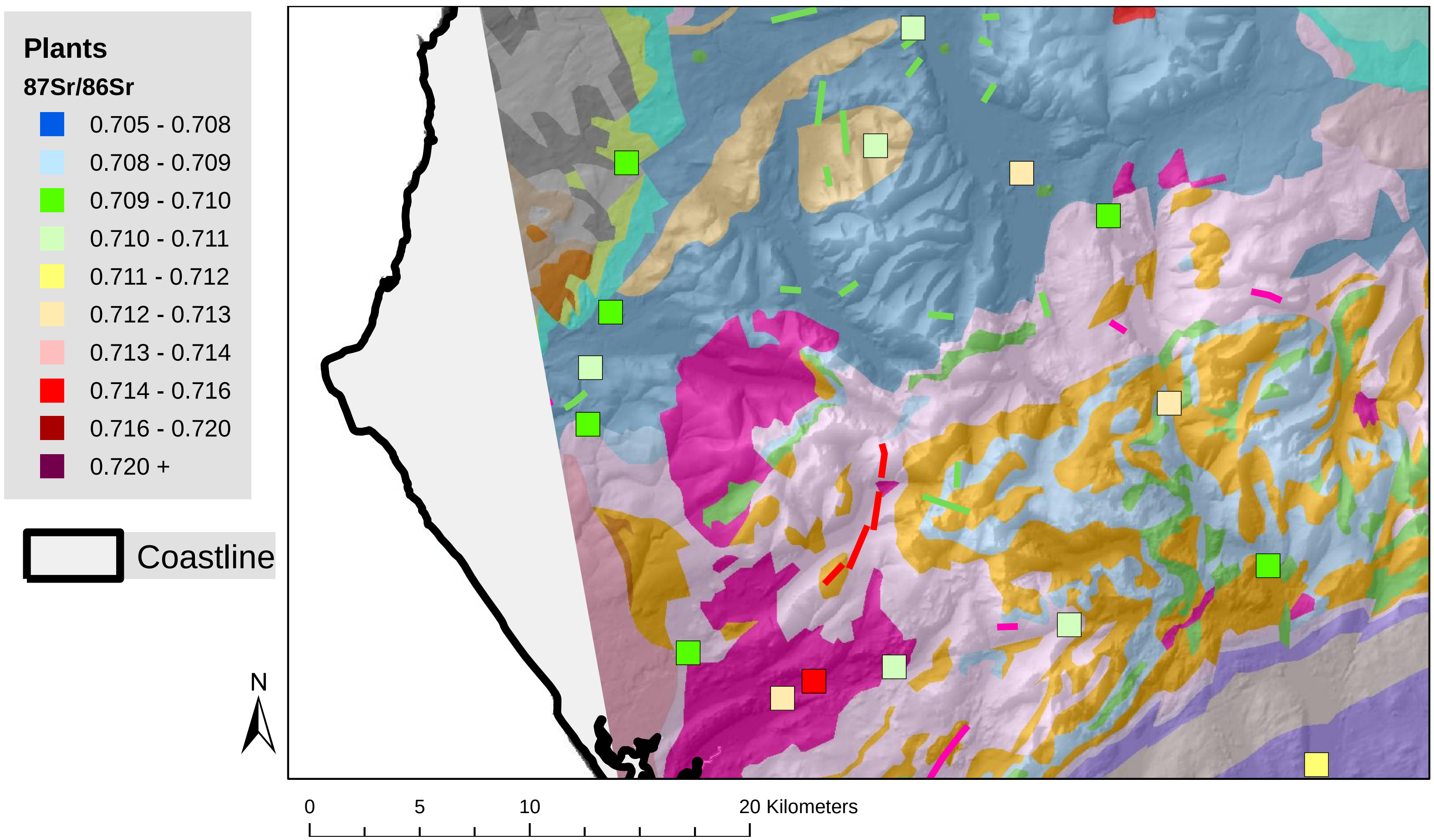


Figure 4.7.1 The plant $^{87}Sr/^{86}Sr$ from across the Lake District study area, alongside GIS data of the 1:625000 Bedrock Geology map (BGS, DiGMapGB, 2007). The main legend for the bedrock geology can be seen in Figure X. The diamond represents the dentine sample Bees-10bd from Knüsel *et al.* (2010), it has the same colour and value scheme as the plant $^{87}Sr/^{86}Sr$.

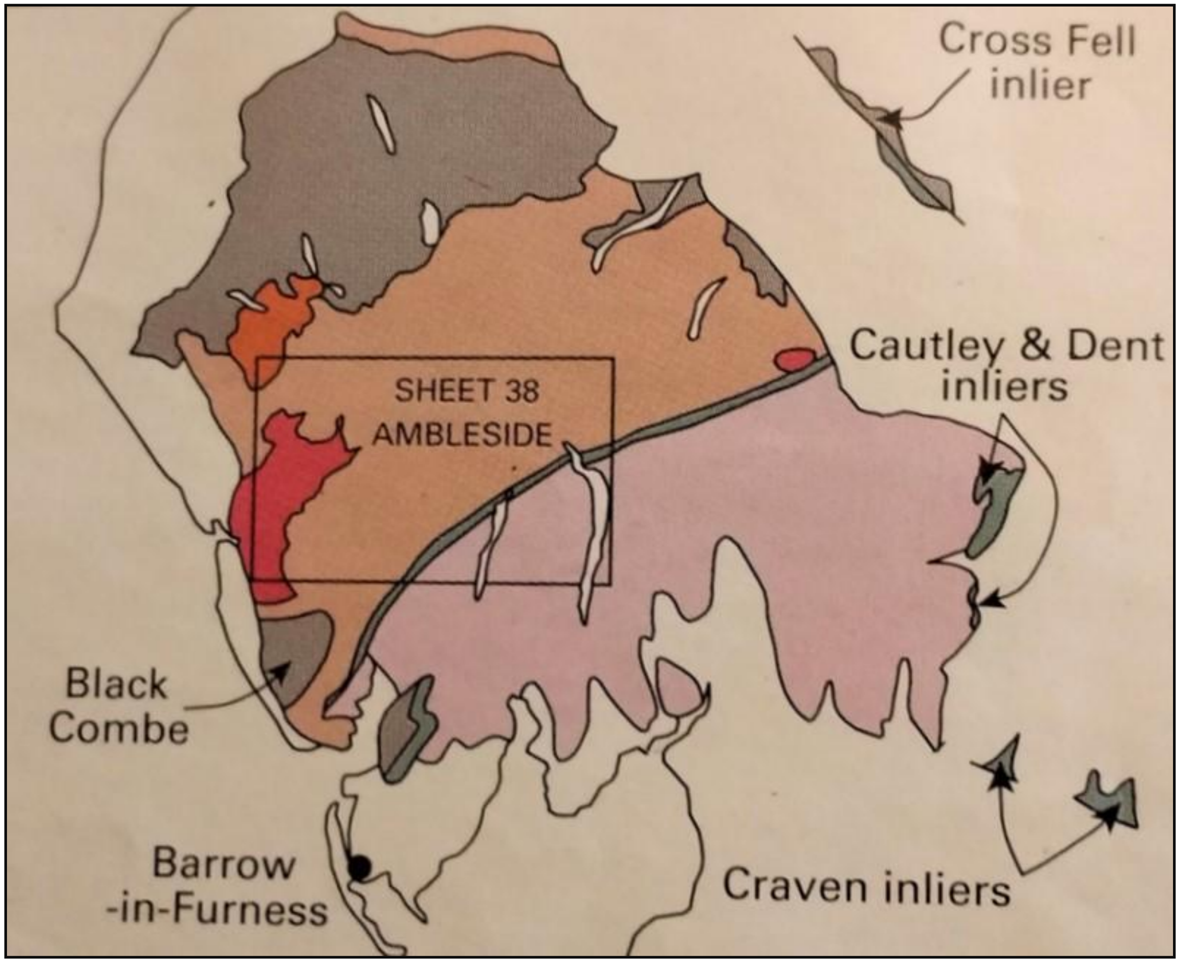


Figure 4.7.2. a section of Figure 1 in Millward *et al.* (2000, p.ii). A simplified summary of the geological bedrock of the Lake District Lower Palaeozoic inlier. The grey represents the Ordovician Skiddaw Group, the light brown represents the Ordovician Borrowdale Volcanic Group, the dark green/grey and the light pink represent the Silurian Windermere Supergroup. The dark pink represents Ordovician Eskdale intrusion (mainly) and the orange represents the Ordovician Ennderdale intrusion.

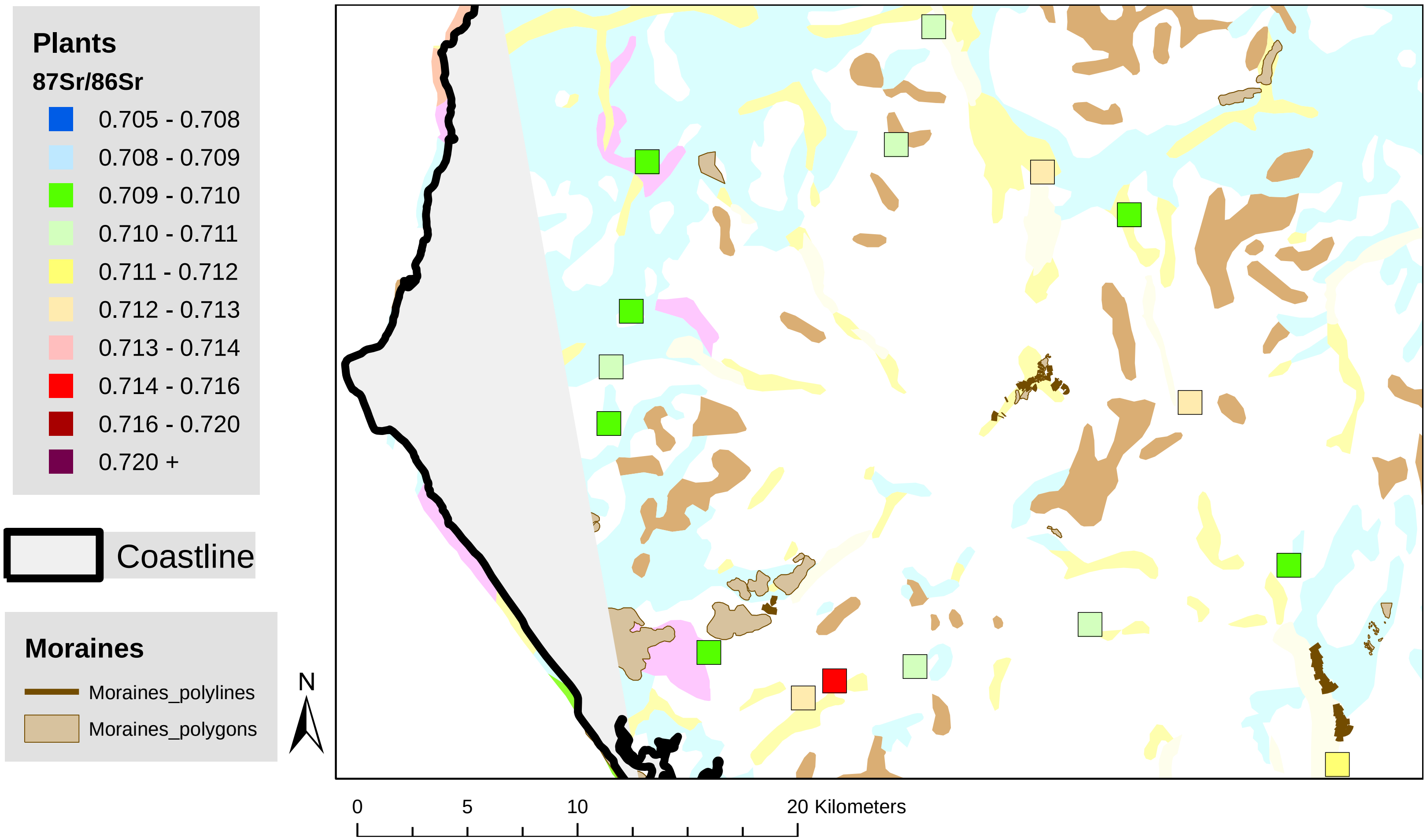


Figure 4.7.3 The plant $^{87}Sr/^{86}Sr$ from across the Lake District, alongside GIS data of the 1:625000 Superficial Geology map (BGS, DiGMapGB, 1977) and BRITICE (Clark *et al.*, 2004; 2017). The legend for the Superficial Geology can be seen in Figure X.

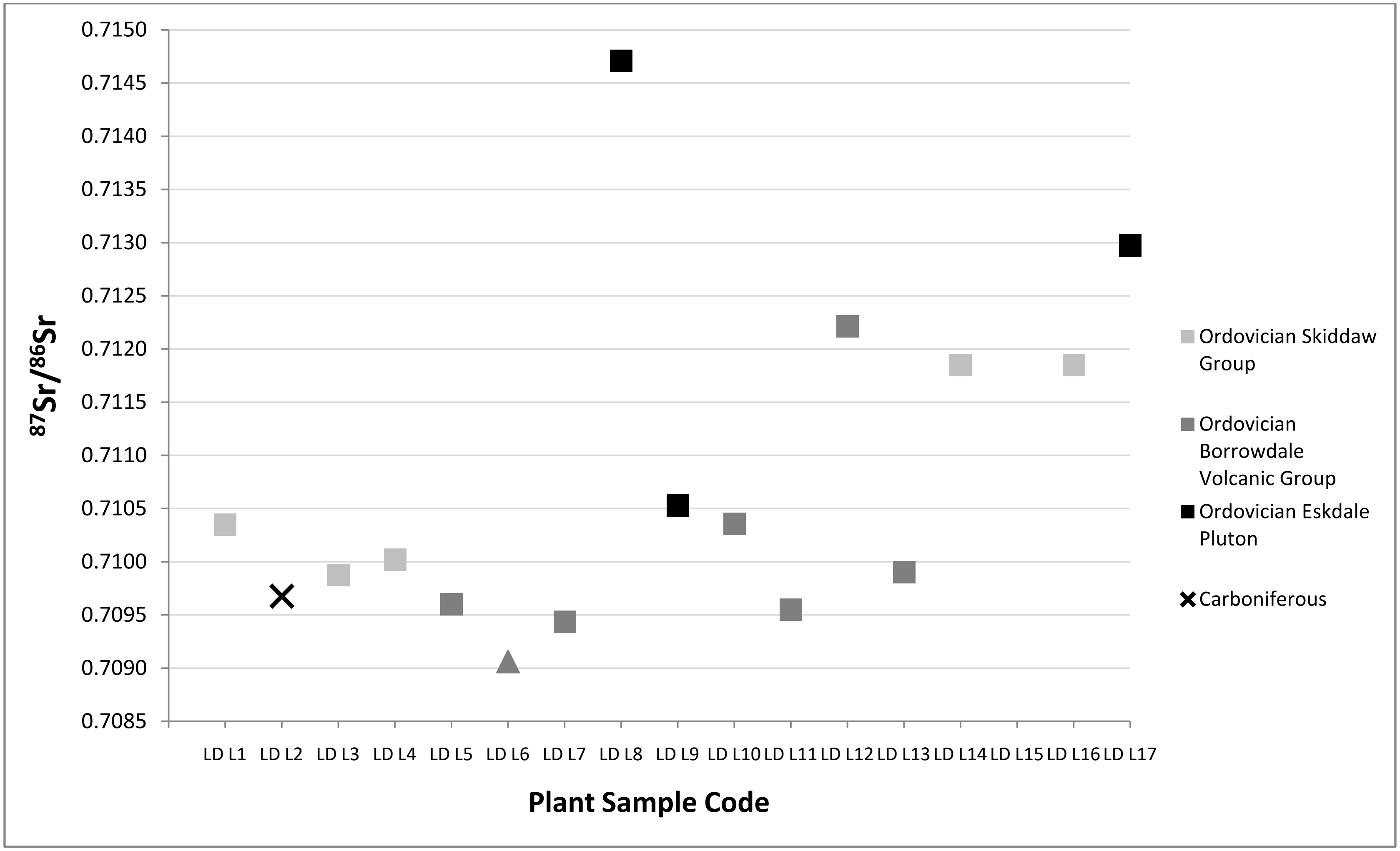


Figure 4.7.4. The plant $^{87}Sr/^{86}Sr$ collected from across the Lake District study area, based on the age of the main bedrock geology from which they were taken.

5. The Scottish Sr-isotope biosphere: The Cairngorms National Park

The highest biosphere $^{87}Sr/^{86}Sr$ seen in Britain, with values >0.720, all occur in Scotland. These values >0.720 are produced by one plant sample growing on the Cairngorm Pluton (Evans *et al.,* 2010), two plant (Evans *et al.,* 2010) and one water sample (Montgomery *et al.,* 2006) on the Precambrian Dalradian Supergroup surrounding the Cairngorm mountain range, and one water sample on the Precambrian gneisses from the Outer Hebrides (Evans *et al.* 2010) (areas in red, Figure 1.1 in chapter 1). A few of these samples on the Dalradian metamorphic rocks have been described as 'hotspots' as there are currently no obvious lithological reasons for their high values (Evans *et al.,* 2010, p.2). In contrast to England and Wales, Scotland also regularly produces biosphere $^{87}Sr/^{86}Sr$ >0.714. Given that a lot of the bedrock geology in Scotland dates to the Precambrian, the lithologies have had the time needed to produce high $^{87}Sr/^{86}Sr$ in the bedrock, e.g. through β-decay of ^{87}Rb, although whether the lithologies have an initial high ^{87}Rb concentration also needs to be considered (chapter 2, section 2.4). There are also many large igneous intrusions, dating to the late Silurian to early Devonian, in Scotland, particularly in the Grampian terrane, which add further potential for high $^{87}Sr/^{86}Sr$ >0.714 in the biosphere.

However, the instances of biosphere $^{87}Sr/^{86}Sr$ >0.714 are sporadic, occurring alongside much lower values over relatively short distances (<10km transect) or having been sampled in low density over large distances (>50km transect). One sporadic example occurs on the Isle of Skye in Scotland. Here the $^{87}Sr/^{86}Sr$ of 28 plant samples ranged from 0.70500 to 0.71996 over an island with an area of c.1700km^2 (Evans *et al.,* 2009; Evans *et al.,* 2010). River water and modern animal remains from across Skye also produced $^{87}Sr/^{86}Sr$ values within the above range. The majority of the values analysed by Evans *et al.,* (2009) correspond to the bedrock geology from which they were collected, which again is very varied and encompasses Precambrian gneisses and sandstones to the south, a variety of igneous intrusive and extrusive rocks from the Paleogene of the Cenozoic (~70Ma ago) in the centre of the island, and some Jurassic sedimentary rocks (including limestone) to the far north-east. Seawater (~0.7092) is also another source of Sr to the biosphere around the coast of this island. Overall, the highest plant $^{87}Sr/^{86}Sr$ values range from 0.716 to 0.720 (n=6) and occur around the base of the granitic outcrops in the centre of the island. However, these values are outweighed (in terms of number of values) by the variety of lower plant $^{87}Sr/^{86}Sr$ values obtained from elsewhere in the Isle of Skye ($^{87}Sr/^{86}Sr$ = 0.7050 - 0.7118, n=22). Also, the four fauna reported in Evans *et al.,* (2009) do not display high $^{87}Sr/^{86}Sr$, recording values at 0.70778, 0.70798, 0.70801 and 0.70916.

The Highlands, north-west of the Great Glen Fault and covering an area of approximately 12,500km^2, is assigned the Sr-isotope package with $^{87}Sr/^{86}Sr$ = 0.713 - 0.72, coloured pink on the Sr-isotope biosphere map of Britain (Evans *et al.,* 2010). This isotope domain package is deemed to be the most appropriate for this area considering the Precambrian bedrock lithologies and their heterogeneous nature. However, the assignment of this package is based on eight plant and water samples, with a mean of 0.7165 ±0.0020 (1SD: Evans *et al.,* 2010). These were mainly collected from around Loch Shin, within 20km of each other. The Cairngorms National Park is another area in Scotland that has low density of samples for the area covered. The limitations of the Sr-isotope data are made very clear in Evans *et al.* (2010): there was limited and non-systematic sample coverage of Britain which has lead to areas with little or no coverage being extrapolated from others (see Evans *et al.,* 2010 supp material for further details).

This chapter focuses on the plant $^{87}Sr/^{86}Sr$ data collected from across the Cairngorms National Park (Figure 1.3 in chapter 1). Currently, there is limited biosphere $^{87}Sr/^{86}Sr$ data available from the Cairngorms National Park , but what has been published ranges from 0.7134 to 0.7266, (n= 9) (Evans *et al.,* 2010) and the data mainly derive from the area of Glenmore and on the Cairngorm Pluton. One of the aims of this study is to see whether such high values are reproducible in the biosphere of the Cairngorms National Park. Therefore, mixed plant samples were collected across a transect from Blairgowrie, in the county of Perth, to Grantown-on-Spey, in the county of Moray (approximately a 144km transect). Samples were also collected from the north of the Cairngorms mountain range in the area around Chapeltown, in the county of Moray, and Glenmore (near to Aviemore) in the Scottish Highlands (see Figure 1.3 in chapter 1, for the position of the place names mentioned).

5.1. Geological Summary of the Cairngorms National Park

The bedrock geology of Cairngorms National Park is detailed below and can be viewed in Figure 5.1, alongside the plant $^{87}Sr/^{86}Sr$ data collected in this chapter. The Blairgowrie to Grantown-on-Spey transect is large, covering 144km, so many of the descriptions below have been summarised and split under geological age subheadings to allow for easier reading. The majority of the plant samples collected were taken from the underlying Dalradian Supergroup of the Precambrian and the late Silurian to early Devonian igneous intrusions forming the Cairngorm mountain range. The latter igneous intrusions will be referred to as just Silurian for simplicity from here on in. The majority of the bedrock geology in the Cairngorms National Park are overlain by a variety of different Quaternary superficial deposits and can be viewed in Figure 5.2, alongside the plant $^{87}Sr/^{86}Sr$ data collected in this chapter.

The Precambrian bedrock geology that makes up the basement of Scotland is divided into five terranes. A terrane is a large proportion of crustal geology that is exotic with respect to the geology either side of it (Trewin & Rollin, 2002, p.1-2). Most of the study transect covered in this chapter lies in the Grampian terrane (also known as the Grampian Highland terrane), which is situated north of the Highland Boundary Fault and south of the Great Glen Fault (Figure 5.3). Like the other terranes in Scotland, the Grampian terrane has undergone a long geological history of intrusive magmatism, deformation and metamorphism. The first major orogenic activity that is important to note was the Grampian event. This event occurred in the Mid Ordovician (often split into four phases or episodes), along with the intrusion of several suites of plutonic rocks in the north-east of the terrane (Strachan *et al.,* 2002, p.104-105, 107, 112-115). The metamorphism caused was regional, with low grade greenschist-facies in the south-west, through to medium-grade epidote-amphibolite to predominantly amphibolite-facies to the north-east (Trewin & Rollin, 2002, p.8-9; Strachan *et al.,* 2002, p.96, 114-115). The orogenic activity that occurred in the late Silurian to early Devonian, known as the Caledonian orogeny, was also very important as it included the intrusion of a supersuite of plutonic rocks into the Grampian terrane (Highton, 1999, p.57-58; Strachan *et al.,* 2002, p.134-143), which includes the Cairngorm suite, which forms the majority of the Cairngorms mountain range in the National Park.

5.1.1. Precambrian (Neoproterozoic) to Cambrian

The Grampian terrane is dominated by the Precambrian lithologies of the Dalradian Supergroup, a well-differentiated sequence of mainly metamorphic marine mud-, silt-, sand- and limestones, which can be divided into the Grampian, Appin, Argyll and Southern Highland Groups. The Dalradian dates between *c.* 800Ma - 509Ma, passing from the Neoproterozic into the Early Cambrian and was controlled by basin faulting (to create accommodation space) and a changing sediment supply, with some volcanic and igneous activity, during the breakup of the late Precambrian supercontinent Rodinia and formation of the Iapetus Ocean. Much of the Dalradian Supergroup throughout the study transect has been affected by medium-grade metamorphism (amphibolite-facies: Trewin & Rollin, 2002, p.8-9; Strachan *et al.,* 2002, p.96, 114-115). Some of the beds within this Supergroup are the equivalents to the Precambrian rocks over in Norway (the Loch na Cille Boulder Bed in the lower part of the Southern Highland Group is comparable to the Varanger Tillite of Norway: Trewin & Rollin, 2002, p.8-9), however the majority correlate to those in Greenland and Newfoundland (relating to the Neoproterozoic continent of Laurentia: Strachan *et al.,* 2002, p.91-92).

The Grampian Group is the oldest within the Dalradian, with outcrops being restricted to the Central Highlands of Scotland. In terms of the study areas, the Grampian Group is located to the north, north-west and south-west of the Cairngorms mountain range. They are poorly exposed and no formal lithostratigraphy exists, being the subject of ongoing research (Highton, 1999, p.12; Strachan *et al.,* 2002, p.96-97). In Highton (1999, p.12-23) local names are adopted when there are mappable units and so the Grampian Group is sub-divided into the Grantown Formation, Nethybridge Formation, Pityoulish Formation and Coylumbridge Formation, along with the Ord Ban Subgroup and Feshiebridge Formation that have uncertain stratigraphical positions. Overall, the Grampian Group is a succession of predominantly micaceous psammitic lithologies (granular quartz-feldspar-biotite rocks with well developed planar foliation), with some occasional semipelite and quartzite beds and local metacarbonate and calc-silicate rocks and metabasic components (mainly in the Grantown Formation and Ord Ban Subgroup: Highton, 1999, p.12-23).

The Appin Group crops out across the whole of the Grampian terrane and comprises of three subgroups: the Lochaber, Ballachulish and Blair Atholl. The constituent formations within these subgroups can be correlated throughout the whole of the Grampian terrane. They show a depositional change from siliciclastic-dominated alternating successions of psammite and quartzite with minor semipelite and pelite (and rare metacarbonates) of the Lochaber subgroup (similar to the lithologies of the Grampian Group above), to the deep water mud and carbonate sedimentation of the Ballachulish and Blair Atholl subgroups. These latter subgroups mainly consist of calc-silicate rocks and psammites with dolomitic and pure calcic limestones, interbanded with graphitic slates and pelites. The Blair Atholl subgroup in the area around the village of Tomintoul can also contain volcaniclastic debris and minor tuff horizons (Smith *et al.,* 2002, p.3-4, p.21-25; Strachan *et al.,* 2002, p.100-101).

The Argyll Group is differentiated on the basis of lithology and environmental conditions at the time of deposition, and is divided into four subgroups: the Islay; Easdale; Crinan; Tayvallich. Overall, the group records the onset of renewed instability in the marine depositional environment by rapid basin deepening (Smith *et al.,* 2002, p.3-4, Strachan *et al.,* 2002, p.101). This sees a return to lithologies like psammite and quartzite being dominant in the Islay subgroup, with a distinct tillite or 'boulder bed' unit (a sequence of sand-, siltstone and conglomerate) at its base, known as the Port Askaig Tillite Formation, which represents a brief episode of glacial deposition (Smith *et al.,* 2002, p.3-4, 26; Strachan *et al.,* 2002, p.101). This is then followed by the Easdale subgroup, consisting of a wide range of finer-grained lithologies including graphitic pelite, semipelite associated with pebbly quartzite, hornblende schist, calcsilicate-rock, limestone and sheets of basic meta-igneous rocks of varying abundance, indicating sporadic basic volcanism (Smith *et al.,* 2002, p.3-4, 26-36; Strachan *et al.,* 2002, p.101-103). The Crinan subgroup is characterized by individually thick formations and metamorphosed turbiditic facies (a fining up-ward sequence of conglomerates to shales; Strachan *et al.,* p.102-103). Across the study transect, the main lithologies in the Crinan subgroup are gneissose semipelites and pelites with subordinate quartzite, psammite, calcsilicate rocks and limestone. This subgroup was particularly prone to migmatization (partial melting during metamorphism; Smith *et al.,* 2002, p.37-38). The overlying Tayvallich subgroup is dominated by carbonates with inputs of siliciclastic and volcaniclastic material, intervened with graphitic pelites and local sheets of mafic lavas and mafic and felsic tuffs (Smith *et al.,* 2002, p.39-43; Strachan *et al*., 2002, p.101-103). Precambrian emplacement of basaltic, doleritic and minor ultramafic sheets (but also sills and lenses) are dominant within the Argyll Group and are mainly found in the Ballater district (BGS, 1995, Sheet 65E; Smith *et al.,* 2002, p.3-4, 50-53).

The Southern Highlands Group marks a return to rapid basin deepening, being a succession of coarse-grained turbiditic and volcaniclastic sedimentary rocks. The lithologies are mainly metagreywackes, peletic slates and phyllites, thin limestone beds and locally interbedded with a series of units rich in chlorite and epidote known as the Green beds (a mixture of siliciclastic and mafic igneous debris: Smith *et al.,* 2002, p.44-49; Strachan *et al.,* 2002, p.103). The Loch na Cille Boulder Bed in the lower part of the Southern Highland Group, described previously, is not present in the study areas, instead being found further south in the Grampian terrane, south-east of the Great Glen Fault (Trewin & Rollin, 2002, p.8-9). Sedimentation of the Southern Highland Group was halted by the Grampian orogenic event which affected all of the Dalradian Supergroup (Strachan *et al.,* 2002, p.104-105).

5.1.2. Ordovician to Silurian

Around the town of Grantown-on-Spey, the northern-most point of the study transect, intrudes the Grantown Pluton. This pluton occupies an area of 25km^2, but only part of it crops out within the Aviemore district. It is mainly obscured by extensive Quaternary glacial deposits. The Grantown Pluton consists of a suite of granitic igneous rocks, mainly fine to medium grained biotite granite, dating to c.470Ma (Highton, 1999, p.50-56). At similar date, a suite of mafic and ultramafic rocks intruded in the district of Ballater and are part of a widespread event in basic magmatism in north-east Scotland known as the Younger Basics. They vary more in lithology than the Precambrian mafic rocks, including metadiorite, metagabbro, amphibolite, hornblendite, pyroxenite and serperntinite (Smith *et al.,* 2002, p.3-4, 53-54). These were intruded into the older Dalradian Supergroup during the deformation and metamorphism of the Grampian event (Strachan *et al.,* 2002, p.112).

5.1.3. Silurian to Devonian

The end of the Caledonian orogeny was marked by uplift and extensive granitic plutonic activity, occurring in the late Silurian and into early Devonian. This is when the 'Caledonian granite' supersuite, calc-alkaline in nature and typical of continental arc environments, intruded into the Grampian terrane. This supersuite is further split into the Argyll, Southern Scotland and Cairngorm suites, in which the latter is the most important for this study (Highton, 1999, p.57-58; Trewin & Rollin 2002, p.9). The Cairngorm suite is easterly trending and forms the majority of the Cairngorms mountain range in the Cairngorm National Park (Figure 5.4). This suite consists of evolved mozograntic plutons, being quite distinct from the other suites, with low Ti, P, Sr and K/Rb and high Rb, Th and U (Highton., 1999, p.57). Near to Aviemore and Glenmore are the Monadhliath Pluton, which forms the Geal-charn Mor mountain, and the Cairngorm Pluton, which forms the majority of the Cairngorms mountains (Figure 5.4). Both of these plutons have similarities with one another. The Monadhliath Pluton has two major granitic types, the coarse-grained pink, locally porphyritic biotite granite mainly to the south and east of the pluton and the western finer-grained, non-porphyritic, biotite poor granite. There are a further two minor components that occur across the pluton, a weakly porphyritic microgranite and a porphyritic aplitic microgranite. The coarse-grained granite has yielded a whole rock Rb-Sr age of 419 ±5Ma (Harrison & Hutchison, 1987). The Cairngorm Pluton is the largest within the Cairngorm suite, covering an area of ~365km^2 and consists of six granitic phases, although only four occur within the Aviemore district. They include: the Main Granite, a medium to coarse-grained non-porphyritic biotite granite (with three textural facies); the Porphyritic Aplitic Microgranite, which is grey-pink in colour, medium-grained and wealkly porphyritic; the Carn Bàn Mor Granite, a fine to medium-grained biotite granite with conspicuous feldspar megacrysts; the Granite Porphyry, similar to the Porphyritic Aplitic Microgranite but with a greater abundance (up to 50% of rock volume) and size (up to 25mm) of quartz and feldspar phenocrysts. All these phases are compositionally similar, with biotite being ubiquitous (and apatite being a predominant accessory mineral), but differ texturally and have undergone some hydrothermal alteration (Highton, 1999, p.68-72).

Heading eastwards is the Glen Gairn Pluton, the Lochnagar Pluton and the Ballater Pluton, as well as the diorite-granodiorite Abergeldie Complex (Figure 5.4). The Abergeldie Complex consists mainly of quartz-diorite with minor tonalite, granodiorite and confined white granite. This complex is consanguineous with the granites of the Glen Gairn and Lochnagar Plutons, showing compositional links to both plutons (Smith *et al.,* 2002, p.82-91). The Glen Gairn Pluton can be split into the Glen Gairn Granite, which is typically medium to coarse-grained and highly xenolithic with inclusions of the surrounding Abergeldie Complex and metasediments, and the Glen Gairn Leucogranite, a coarse-grained pink biotite grainte (very similar to the Cairngorm or Monadhliath granites). The Lochnagar Pluton covers an area of approximately 150km^2 in which the granites are split into three main phases as well as several different microgranites. Phase one are characteristically coarse-grained and porphyritic granites and were originally a 15km across pluton intrusion. The phase two granites subsequently cored a 12x9km pluton into phase one and mainly consists of medium to coarse-grained, inequigranular, unfoliated grey and pink leucocratic rocks (Smith *et al.,* 2002, p.92-97). This phase has been dated to 425 ±4Ma by U/Pb age determinations (Smith *et al.,* 2002, p.3). Phase three is the most evolved chemically mainly being white and pink equigranular leucocratic biotite granite, which also intrudes into the phase one granites to the south and west, however their relation to phase two granites are not known (Smith *et al.,* 2002, p.92-97). Phase three dates significantly younger than phase two at 417 ±1Ma by U/Pb age determinations (Smith *et al*., 2002, p.3). Phase one and two are cut by several bodies of microgranites, most of which appear to be compositionally related to their hosts and so are believed to belong to the same intrusive episode as their host (Smith *et al.,* 2002, p.92-97).

Further east is the larger Ballater Pluton, being approximately 30km^2. This pluton contains two granite lithotypes. The first is mainly pink in colour, medium to coarse-grained, sparsely porphyritic to porphyritic, with K-feldspar megacrysts (up to 25mm) and is based in the central and north-western parts of the pluton. The east part of the pluton has granites that are still very similar to above, but become very coarse-grained with even larger K-feldspar megacrysts (>50mm: Smith *et al.,* 2002, p.97-100).

Many minor intrusions mainly dating to the late Silurian, including igneous dykes, sheets and veins, form a significant component throughout the Grampian terrane. They are mainly underformed microdiorites and lamprophyres (which are ultrapotassic igneous rocks with phenocrysts of mica and amphibole) and are believed to be coeval with the 'Caledonian granite' supersuite (Smith *et al.,* 2002, p.113-117; Strachan *et al.,* 2002, p.141). They can form notable concentrations, as in north-west and south-west segments of the Ballater district and also range in thickness (centimetres to metres) and length (metres to kilometres: BGS, 1995, Sheet 65E; Smith *et al.,* 2002, p.113-117).

The cooling, uplift and erosion at the end of the Caledonian orogeny continued regionally before the deposition of the Old Red Sandstone (ORS) sequences in Scotland, although the Lower ORS can contain volcanic lavas and volcaniclastic rocks when they coincided (Strachan *et al.,* 2002, p.146; Trewin & Rollin, 2002, p.10-11; Trewin & Thirlwall, 2002, p.213-218). There is a transition from marine to non-marine deposition reflecting semi-arid conditions in the ORS, but differ in time in different areas across Scotland dependant on when the two major basins, the Orcadian or Midland Valley, became isolated from any marine influences (Trewin & Thirlwall, 2002, p.213-218). The beginning of the study transect is partially based on the Lower ORS of the Midland Valley basin and crosses the Highland Boundary Fault. This is to the north of the town of Blairgowrie, where the Arbuthnott-Garvock Groups dominate, consisting of conglomerates and sandstones containing volcanic clasts and tuffs, with subordinate volcanic lavas. The composition of these igneous components can vary from felsic to mafic, the lavas however are mainly basaltic andesites (BGS, 1999, Sheet 56W; Trewin & Thirlwall, 2002, p.218-222). Further to the north in the Cairngorms National Park, past the Glen Gairn and Cairngorm Plutons, around the village of Tomintoul is a ORS outlier based between the two major ORS basins, but drainage here was northwards into the Orcadian area. This outlier is part of the Lower ORS and is dominated by alluvial fan conglomerates that pass northwards into sandstone (Trewin & Thirlwall, 2002, p.213, 228).

5.1.4. Quaternary Superficial Deposits

Throughout the Quaternary, Scotland has experienced many different environments, from fully glacial to tundra during glaciations, to boreal (equivalent to modern pine/spruce forests of Scandinavia) and temperate during interglacials. The glacial stages have had a major influence of the Scottish landscape, through glacial erosion of valleys and sea lochs have progressively deepened, while plateau tops have preserved tors and relics of the Tertiary period. The movement of ice sheets from each glaciation has resulted in striated and smoothed bare rock surfaces in the upland areas and the deposition and formation of drumlins of till in the lowlands, with the outwash from the ice sheets also having produced extensive glaciofluvial deposits (Trewin & Rollin, 2002, p.15-16). The Quaternary stratigraphy is extensive and complex with the whole of Scotland being covered by or near to some form of superficial deposit.

The majority of the Quaternary superficial deposits date to the last glacial stage, termed the Devensian in Britain. However there are several features within the landscape that have been formed because of repeated glaciations. The intensity of glacial erosion contrasts from the western Highlands, with its highly indented fjord-coastline, deep troughs (U-shaped valleys) and sharp ridges, to the eastern Highlands with its smoother mountain outlines and coastline. The Grampian Highlands contains a series of major troughs that radiate from Rannoch Moor (found to the south-west of the Cairngorms National Park) and suggests that the area has been a persistent ice sheet centre from which ice flow has radiated during each of the Quaternary glaciations. Corries (the starting point of a glacier) are another glacial feature thought to that have formed through several glaciations, being more numerous and at lower altitudes in the west Highlands compared to the east, although the corries in the east cluster on the Cairngorm mountain range (Highton, 1999, p.4; Boulton *et al.,* 2002, p.411-415; Smith *et al.,* 2002, p.4).

The Devensian glacial stage occurred approximately 120,000 years ago in which the majority of the time Scotland was covered by an ice sheet that centred in the Scottish Highlands and Southern uplands. By the glacial maximum, about 20, 000 years ago, this ice sheet had expanded and merged with other centres and so in its entirety covered the majority of Wales and northern England. There is widespread glacial erosion of the bedrock from this expanding ice sheet across Scotland, which is mainly deposited as till in the lowlands and also includes local rock clasts which give indications of the dispersal of ice flow in the area. Erratics such as Norwegian larvikite and rhomb porphyry are found in several locations along the southern Aberdeen coast, but there is no mention of such erratics being found further inland (Boulton *et al.,* 2002, p.415-422). Other superficial deposits such as alluvium and peat have formed and grown in size more recently, particularly in upland areas of the Aviemore and Ballater district (Highton, 1999, p.4; Boulton *et al.,* 2002 p.428; Smith *et al.,* 2002, p.4). These have also been influenced by human activity since approximately 5000 BP, when extensive deforestation begun in Scotland (Boulton *et al.*, 2002, p.430).

The most dominant superficial deposits across the transect and study areas have been noted in the field-notes of Scotland and can be viewed in the Appendix 2. These are based on the BGS 1:50,000 Superficial/Drift maps where available or the BGS 1:625000 Superficial map (1977).

5.2. Geochemical Survey and Field-notes for the Cairngorms National Park

In August 2014, 25 locations were visited along the study transect from Blairgowrie to Grantwon-on-Spey, as well as five locations around the village of Chapeltown (Ballindalloch, Scotland) and nine locations around Aviemore and Glenmore, north of the Cairngorms mountain range. The weather over the collection period was mainly sunny with strong winds, but was not overly dusty. At least three plants were collected and mixed for each location by the methods described in chapter 3, section 3.2. In some locations the selection of plant species available were limited with, for example, only pine being available. Nonetheless, at least three plants were chosen to be mixed. These plants were also mainly from woodlands. Further information can be seen in the field-notes for Scotland in the Appendix 2. All the mixed plant samples followed the methods for chemical preparation and Sr-isotope analysis outlined in section 3.3 in chapter 3.

5.3. Plant $^{87}Sr/^{86}Sr$ Results

The plant $^{87}Sr/^{86}Sr$ results from across the Cairngorms National Park are displayed in Figure 5.5 (the transect), 5.6 (Chapeltown) and 5.7 (Glenmore). These results are also displayed against the bedrock geology and Quaternary superficial deposits in Figure 5.1 and 5.2 respectively.

Altogether, the metasediments of the Precambrian Dalradian Supergroup have mean plant $^{87}Sr/^{86}Sr$ = 0.7123 ±0.0059 (n=24 , 2SD). If this Supergroup is further split, the mean plant $^{87}Sr/^{86}Sr$ = 0.7150 ±0.0058 (n=9, 2SD) for the Grampian Group, 0.71161 ±0.00671 (n=9, 2SD) the Appin Group, 0.7122 ±0.0042 (n=4, 2SD) for the Argyll Group and the Southern Highlands Group has values of 0.71093 (SCOT L3) and 0.71151 (SCOT L5). The mixed plant sample SCOT L4 is located on a Precambrian metamorphic igneous intrusion, predominantly mafic in composition and has $^{87}Sr/^{86}Sr$ = 0.71066 (Figure 5.5).

The Ordovician Grantown Pluton, a suite of granitic igneous rocks, has a plant $^{87}Sr/^{86}Sr$ of 0.71463 (SCOT L25), while the granitic rocks of the Silurian Cairngorm suite have plant $^{87}Sr/^{86}Sr$ = 0.7132 ±0.0046 (n=6, 2SD). The Silurian Abergeldie Complex, made up of predominately diorites and granodiorites, has a plant $^{87}Sr/^{86}Sr$ of 0.71064 (SCOT L14). Lastly, the Devonian ORS of the Midland Valley basin have plant $^{87}Sr/^{86}Sr$ at 0.71267 (SCOT L1) and 0.71100 (SCOT L2), while those based on ORS outlier, around the village of Tomintoul, has plant $^{87}Sr/^{86}Sr$ at 0.71094 (SCOT CTL1) and 0.71656 (SCOT CTL2). Overall, 13 mixed plant samples record radiogenic values >0.714 from across the Cairngorms National Park in Scotland. The plant $^{87}Sr/^{86}Sr$ results are further discussed below.

The mixed plant samples SCOTL6 and L9 from the transect (Figure 5.5) were both unsuccessful on their initial and repeated run on the TIMS for Sr-isotope analysis at the NIGL (Keyworth). Both of these mixed plant samples were located on the Precambrian Dalradian Supergroup, specifically the Argyll and Appin Groups respectively. As several other samples were taken from the Dalradian Supergroup, re-collection of new plant samples from these two locations was deemed unnecessary.

5.4. Discussion of plant $^{87}Sr/^{86}Sr$ from across the Cairngorms National Park

The majority of the mixed plant samples taken from across the study transect and from the study areas surrounding the village of Chapeltown and Glenmore and Aviemore correlate well with the bedrock substrate they overlie or can be explained by other geological inputs. These will be discussed in the sections below.

5.4.1. The plant $^{87}Sr/^{86}Sr$ on the Cairngorm Suite

Evans *et al.* (2010) report the Cairngorm, Etive and Angus granites of Scotland as having a biosphere $^{87}Sr/^{86}Sr$ = 0.7175 ±0035 (n=11, 1SD). For the Cairngorm suite alone, the Cairngorm Pluton has two water samples with $^{87}Sr/^{86}Sr$= 0.71571 (Aberd-2) and 0.71568

(Aberd-4) and a plant sample with the value of 0.71672 (EBP-46a) (Evans *et al.,* 2010), while the Ballater Pluton has a water sample with $^{87}Sr/^{86}Sr$ = 0.71463 (JMW 18: Montgomery *et al.*, 2006). The Cairngorm suite in this study produced plant $^{87}Sr/^{86}Sr$ = 0.7132 ±0.0046 (n=6, 2SD). The plant sample SCOT L17 and SCOT L18 both have $^{87}Sr/^{86}Sr$ <0.713, at 0.71135 and 0.71114 respectively, and do not compared well with other biosphere $^{87}Sr/^{86}Sr$ >0.713 on the Cairngorm suite. One reason for their low $^{87}Sr/^{86}Sr$ values could be the locations. Both these mixed plant samples were taken from the outskirts of the pluton, so there is a possibility that the nearby Appin Group of the Dalradian has contributed Sr to the biosphere in this area, producing lower values than expected. However, there are plenty of exposed granitic rocks present in the vicinity at both locations making this hypothesis improbable. The location of SCOT L17 is also noted as being boggy (Appendix 2). This suggests instead, that the soil at both locations is saturated in rainwater, leading to a higher input of Sr from atmospheric sources and therefore lower $^{87}Sr/^{86}Sr$ values being bioavailable to the plants in the area. If these values are removed from the Cairngorm suite mean in this study, then the plant $^{87}Sr/^{86}Sr$ = 0.7152 ±0.0010 (n=4, 2SD). If the values from Evans *et al.* (2010) are included too, then the Cairngorm suite has an overall mean biosphere $^{87}Sr/^{86}Sr$ = 0.7155 ±0.0014 (n=8, 2SD).

The sample SCOT L16 on the Ballater Pluton, with $^{87}Sr/^{86}Sr$ of 0.71487, compares very well with the water sample from the same pluton at 0.71463 (JMW 18: Montgomery *et al.* 2006). However, the sample SCOT GL4 on the Cairngorm Pluton, with $^{87}Sr/^{86}Sr$ of 0.71360, is lower by approximately -0.002 than the plant, at 0.71672 (EBP-46a), and water samples, 0.71571 (Aberd-2) and 0.71568 (Aberd-4), on the same pluton in Evans *et al.* (2010).

Water samples have been shown to produce higher values than other biosphere proxies on the same bedrock in Scotland. For example, the granite and gneisses of the Outer Hebrides have water $^{87}Sr/^{86}Sr$ = 0.71785, 0.71821 and 0.72335 (Evans *et al.,* 2010), but these high values have not repeated in the overall biosphere of the Outer Hebrides, which instead reflects the sea-spray and Quaternary machair deposits (~0.70925 - 0.71025: Montgomery *et al.,* 2003; Evans *et al*., 2010). However, this does not account for the plant sample EBP-46a, on the Cairngorm Pluton, at 0.71672 (Evans *et al.,* 2010), which is more radiogenic than the water samples on the same pluton and so it is deemed that the proxy type chosen is not the main reason to why there is difference in $^{87}Sr/^{86}Sr$ value. Instead the plant sample's location may be important here. The plant sample EBP-

46a is at a lower elevation compared to SCOT GL4. The location of SCOT GL4 had sparse vegetation with plenty of exposed granitic rock (Appendix 2), e.g. a typical terrain of a mountain side. The combination of a poor, thin soil, which is potentially saturated due to the higher than average rainfall experienced by the Cairngorms National Park, has resulted in a lower $^{87}Sr/^{86}Sr$ bioavailable to the plants growing on the mountain side.

5.4.2. A aureole of high biosphere $^{87}Sr/^{86}Sr$ around the Cairngorm suite

Although the Cairngorm suite can produce $^{87}Sr/^{86}Sr$ >0.714 (section 5.4.1 above), the highest values in the Scottish biosphere seen in this study have been based on the Precambrian Dalradian Supergroup, specifically the Grampian Group. The majority of these high $^{87}Sr/^{86}Sr$ form an aureole north of the Cairngorm and Monadhliath Plutons, in the area around Glenmore and Aviemore (Figure 5.1 and 5.7). The plant $^{87}Sr/^{86}Sr$ from this study range from 0.71375 - 0.71820 (n=5), while two plant samples at 0.72660 (EBP-48) and 0.71463 (EBP-49), and a water sample at 0.71937 (EBP-47) from Evans *et al.* (2010) are also from the same area. The plant $^{87}Sr/^{86}Sr$ sample of 0.72660 (EBP-48: Evans *et al.,* 2010) has not been reproduced by the mixed plant samples in the same area, the highest value comes from SCOT GL3 at 0.71820 (Figure 5.7) which is a significant difference of -0.0084. If the plant value >0.726 is excluded because of its significant difference in value, the aureole north of the Cairngorm and Monadhliath Plutons has a mean biosphere $^{87}Sr/^{86}Sr$= 0.7174 ±0.0049 (n=7, 2SD).

All of the aureole samples are within 4km of the Cairngorm and Monadhliath Plutons and may be a result of the contact metamorphism and hydrothermally activity that occurred when these plutons intruded into the older Precambrian bedrock. The plant samples collected further away from these plutons (>5km approximately), but still on the Grampian Group, are lower, with a mean plant $^{87}Sr/^{86}Sr$ = 0.7119 ±0.0021 (n=6, 2SD: SCOT L12, SCOT GL1, SCOT GL9 from this study and EBP-14, EBP-45 and HIGH-07 from Evans *et al,.* 2010) and provide further support for this hypothesis. A similar high $^{87}Sr/^{86}Sr$ aureole can be seen in the Church Stretton study area (chapter 4, section 4.4), although the plant $^{87}Sr/^{86}Sr$ are relatively lower. Together these high $^{87}Sr/^{86}Sr$ aureoles are an interesting observation and will be further discussed in chapter 8, section 8.1.2.

5.4.3. The plant $^{87}Sr/^{86}Sr$ on the Precambrian Dalradian Supergroup

The Precambrian Dalradian bedrock from Scotland reported by Evans *et al.* (2010) have mean plant $^{87}Sr/^{86}Sr$ = 0.7097 ±0.0003 (n=4, 1SD) and 0.7127 ±0.0005 (n=9, 1SD), while the Appin Group specifically has a plant $^{87}Sr/^{86}Sr$ =0.7113 ±0.0006 (n=4, 1SD). Altogether, including the results in section 5.3 above, the Dalradian Supergroup in this study have plant $^{87}Sr/^{86}Sr$ = 0.7123 ±0.0059 (n=24, 2SD). The $^{87}Sr/^{86}Sr$ values in this study have a larger range than those reported by Evans *et al.* (2010). However, they include the high biosphere $^{87}Sr/^{86}Sr$ of the aureole around the Cairngorm and Monadhliath Plutons on the Grampian group (section 5.4.2).

The Grampian Group

Not including the plant $^{87}Sr/^{86}Sr$ from the around the base of the Cairngorm and Monadhliath Plutons as they may be the result of a thermal aureole (section 5.4.2), the Grampian group has plant $^{87}Sr/^{86}Sr$ = 0.7119 ±0.0021 (n=6, 2SD: this chapter; Evans *et al.,* 2010), with an elevated value at 0.71418 (SCOT L24) on the Cromdale Hills Quartzite Member of the Grampian Group. Not including the elevated value, the plant $^{87}Sr/^{86}Sr$ of the Grampian Group compare well with the higher plant values of the Dalradian in Evans *et al.* (2010), at 0.7127 ±0.0005 (n=9, 1SD). The elevated value from plant sample SCOT L24 was rooted in exposed bedrock (Appendix 2) and so may have unusual $^{87}Sr/^{86}Sr$, as was seen in the plant sample LD L8 which was also rooted in exposed rock in the Lake District (chapter 4, section 4.10.3.). However, other quartzite formations of the Appin Group, discussed below, also record plant $^{87}Sr/^{86}Sr$ ~0.714 and so value >0.714 may be typical of the biosphere overlying this bedrock lithology.

The Appin Group

The Appin Group, with plant $^{87}Sr/^{86}Sr$ = 0.7116 ±0.0067 (n=9, 2SD), has the most complex plant values than any other group within the Dalradian Supergroup. The area around Chapeltown is a good example (Figure 5.6). This area was chosen as a previous water sample (JMW 23) in Montgomery *et al.* (2006) has a $^{87}Sr/^{86}Sr$ = 0.72065, which reflects the granitic rocks of the nearby Silurian Glenlivet intrusion (BGS, 1995, Solid Geology, Sheet 75E). The plant $^{87}Sr/^{87}Sr$ on the Appin Group surrounding the Glenlivet intrusion had values of 0.70844 (SCOT CTL4), 0.70999 (SCOT CTL3) and 0.71426 (SCOT CTL5). The mixed plant samples have not repeated the high water value >0.720 seen in Montgomery *et al.* (2006). Instead they reflect the bedrock substrate they are situated on rather than the weathering of the Glenlivet intrusion. The lower values <0.710 are on the metalimestone and calcareous metasediments of the Appin Group, while the higher value >0.714 is on the Corryhabbie Quartzite Formation (Figure 5.1).

The highest value on the Appin Group, at 0.71732 (SCOT L23), is located to the north-west of Tomintoul, where the Blair Atholl subgroup can contain volcaniclastic debris and minor tuff horizons (Smith *et al.,* 2002, p.3-4, p.21-25; Strachan *et al.,* 2002, p.100-101). Approximately 2km south of SCOT L23 is SCOT L22, which is on the metalimestone formation and has a plant $^{87}Sr/^{86}Sr$ at 0.70795, showing that the values >0.714 in this area are not consistent over several kilometres.

The bedrock geology of Appin Group is complex, where the main lithologies, being the calcareous metasediments, metalimestone and quartzite, can all occur over 5km distances (see Figure 5.1). The plant $^{87}Sr/^{86}Sr$, however, can be split based on the lithologies, with the exclusion of the mixed plant sample SCOT L23, on the Appin metasediments, with the high value of 0.71732: the metalimestones have plant $^{87}Sr/^{86}Sr$ 0.70795 (SCOT L22) and 70844 (SCOT CTL4); the calcareous metasediments have plant $^{87}Sr/^{86}Sr$ 0.70879 (SCOT L8), 0.70999 (SCOT CTL3) and 0.71007 (SCOT L19); the quartzite have plant $^{87}Sr/^{86}Sr$ 0.71292 (SCOT L11), 0.71426 (SCOT CTL5) and 0.71432 (SCOT L10).

The mixed plant sample SCOT L8 with $^{87}Sr/^{86}Sr$ of 0.70879, on the metasediments of the Appin Group, compares better plant $^{87}Sr/^{86}Sr$ on the metalimestones of the Appin Group at 0.70795 and 70844. Sample SCOT L8 was collected from an area that has been intruded by small Silurian intrusions (such as dykes) which are mafic in composition, as well as having drumlins containing till (Appendix 2). It is therefore possible that the $^{87}Sr/^{86}Sr$ of SCOT L8 reflects the Sr inputs of either, or a combination of: the Silurian mafic intrusions; the Quaternary till, which could easily contain components of a nearby metalimestone formation (see figure 5.1 and 5.2).

The Appin Group reported in Evans *et al.* (2010) has plant $^{87}Sr/^{86}Sr$ = 0.7113 ±0.0006 (n=4, 1SD). The four plant samples were collected from the metasediments of the Appin Group. If combined with the plant $^{87}Sr/^{86}Sr$ data in this study (excluding SCOT L8), the Appin Group metasediments have plant $^{87}Sr/^{86}Sr$ = 0.7108 ±0.0015 (n=7, 2SD).

The Argyll Group

Evans et al. (2010) report plant $^{87}Sr/^{86}Sr$ of 0.71173 (EBP-14), 0.71269 (EBP-22) and 0.71328 (EBP-26) for the Argyll Group. The Argyll Group in this study has a plant $^{87}Sr/^{86}Sr$= 0.7122 ±0.0042 (n=4, 2SD). The lowest plant $^{87}Sr/^{87}Sr$, at 0.70971 (SCOT L7), and highest value, at 0.71465 (SCOT L21) are both on the Argyll Group metasediments, just over 45km apart approximately. However, several quartzite formations were also present within the location of mixed plant sample SCOT L21, at 0.71465, which compares well to other plant $^{87}Sr/^{87}Sr$ on the quartzite formations in the Grampian and Appin Groups above. Therefore the assignment of sample SCOT L21 to the metasediments may have been misidentified. If this is the case, the quartzite formations of the Precambrian Dalradian Supergroup are commonly producing plant $^{87}Sr/^{86}Sr$ ~0.714.

The Southern Highlands Group

The Southern Highlands Group in this study has plant $^{87}Sr/^{86}Sr$ at 0.71093 (SCOTL3) and 0.71151 (SCOTL5). A water sample (EBP-42) with $^{87}Sr/^{86}Sr$ of 0.71274 and two plant samples, EBP-43 and EBP-41, with$^{87}Sr/^{86}Sr$ of 0.70946 and 0.72093 respectively, are also on the Southern Highlands Group (Evans *et al.,* 2010). The latter plant sample, being >0.720, was described in Evans *et al.* (2010) as a 'hotspot' as there is no obvious lithological reason for its high value. If excluding this hotspot value, the Southern Highlands Group has a mean biosphere $^{87}Sr/^{86}Sr$ = 0.7112 ±0.0027 (n=4, 2SD)

5.4.4. The plant $^{87}Sr/^{86}Sr$ of the Lower ORS outlier

Only two mixed plant samples are located on the Lower Old Red Sandstone (ORS) outlier, SCOT CTL1 and SCOT CTL2. Their plant $^{87}Sr/^{86}Sr$ values are significantly different though, at 0.71094 and 0.71656 respectively. Even though they are both on the Lower ORS, specifically sample SCOT CTL1 is on the Conglass Sandstone Formation, while SCOT CTL2 is on the Raebag Sandstone Formation (BGS, 1996, Solid Geology, Sheet 75W). The Conglass Sandstone Formation contains grey sandstones cross-bedded with green siltstones, while the Raebag Sandstone Formation has been described as containing micaceous sandstone with pebbly beds (BGS, 1996, Soild Geology, Sheet 75W). It is improbable that the miceaceous sandstones of the Raebag Sandstone Formation alone would cause a difference of +0.0056 between the two plant $^{87}Sr/^{86}Sr$. The only other difference between the two samples is that SCOT CTL1 was collected from a modern plantation and SCOT CTL2 from an ancient woodland owned by the Crown (in Scotland, ancient woodlands described any woodland that dates from at least 1750 AD: AWI, Scotland, 2010). Potentially the miceaceous sandstones of the Raebag Sandstone Formation and the woodland effect (see chapter 2, section 2.4.3) combined has resulted in the high value recorded for SCOT CTL2.

The mixed plant samples SCOT L1 and SCOT L2, located on the Lower ORS of the Midland Valley Basin, with plant $^{87}Sr/^{86}Sr$ of 0.71267 and 0.71100 respectively. SCOT L1 is slightly higher than expected by the Devonian bedrock in Scotland, with Evans *et al.* (2010) reporting biosphere $^{87}Sr/^{86}Sr$ = 0.7098 ±0.0010 (n=29, 1SD). However, the mean biosphere $^{87}Sr/^{86}Sr$ for the Scottish Devonian bedrock reported in Evans *et al.* (2010) is based on samples located on all the different basins of the ORS and several are near to the coastline of Scotland. Both SCOT L1 and SCOT L2 were taken from the Arbuthnott-Garvock Group of the Lower ORS of the Midland Valley Basin (section 5.1.3), which can contain volcanic clasts and tuffs as well as subordinate lavas, and these may have influenced their plant $^{87}Sr/^{86}Sr$, resulting in higher values than seen by the Devonian bedrock in Evans *et al.* (2010).

5.4.5. Quaternary Superficial Deposits

The Quaternary superficial deposits across the study transect are described in section 5.1.4 and can be seen in Figure 5.2. Most of the mixed plant samples are located on superficial deposits, with glacial till, glacial sand and gravel and alluvium being the most common deposits. Only two mixed plant samples, SCOT L20 and SCOT L21, are not (Figure 5.2). These two samples have been discussed in section 5.4.3 above and their $^{87}Sr/^{86}Sr$ values cannot be explained by a lack of superficial deposits. It is very difficult to interpret whether the superficial deposits have any great influence on the $^{87}Sr/^{86}Sr$ recorded in the Cairngorms National Park because of a lack of comparisons. It is also believed that the majority of the Quaternary superficial deposits will consist of the weathered and eroded components of the local bedrock, and so would be unlikely to be distinguishable by the $^{87}Sr/^{86}Sr$ values recorded, with the possible expectation of the metalimestone formations.

So far the only mixed plant sample likely influenced by superficial deposits is SCOT L8 with $^{87}Sr/^{86}Sr$ of 0.70879, which is on the metasediments of Appin Group, but had plant $^{87}Sr/^{86}Sr$ more reflective of the metalimestones (see section 5.4.2). The glacial till in the area possibly contains material from the metalimestone formation found approximately 2km north of this location, leading to the lower value recorded. However, this value could also be explained by the small mafic igneous intrusions (dating to the Silurian) found in the bedrock of this area (Figure 5.1).

5.5. Concluding remarks for the Sr-isotope biosphere of the Cairngorms National Park

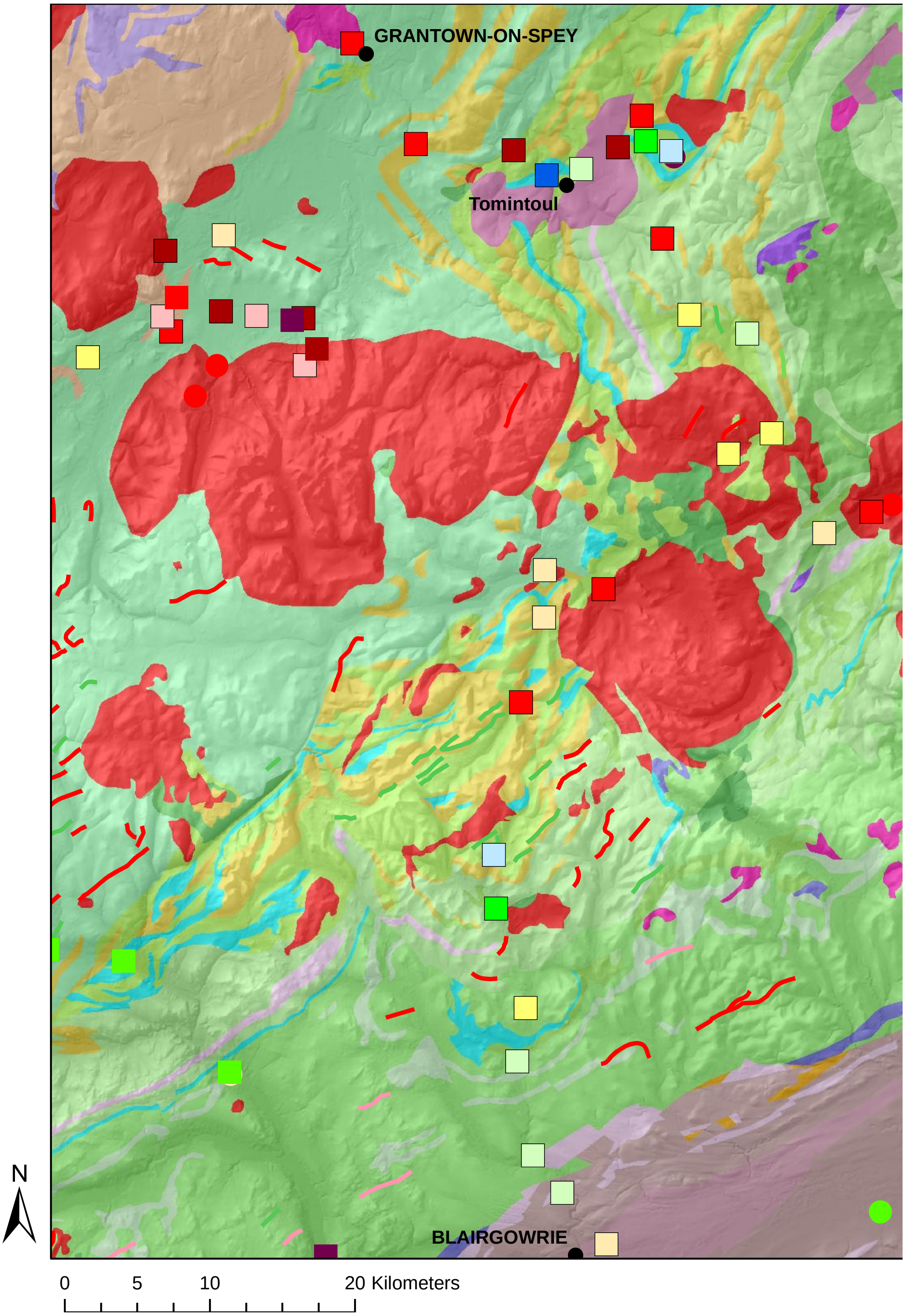
The Cairngorms National Park has produced 13 mixed plant samples with $^{87}Sr/^{86}Sr$ >0.714, but none of these have been able to repeat the values >0.720 seen in Evans *et al.* (2010). The highest $^{87}Sr/^{86}Sr$ obtained in this study is SCOT GL3 at 0.71820. The area north of the Cairngorms suite, around Glenmore and Aviemore has produced an aureole of high $^{87}Sr/^{86}Sr$ (discussed in section 5.4.2.) and highlights an interesting observation between biosphere $^{87}Sr/^{86}Sr$ and the thermal or metamorphic aureoles formed around large igneous intrusions when they intrude into country rock. This will be discussed further in chapter 8, section 8.1.2.

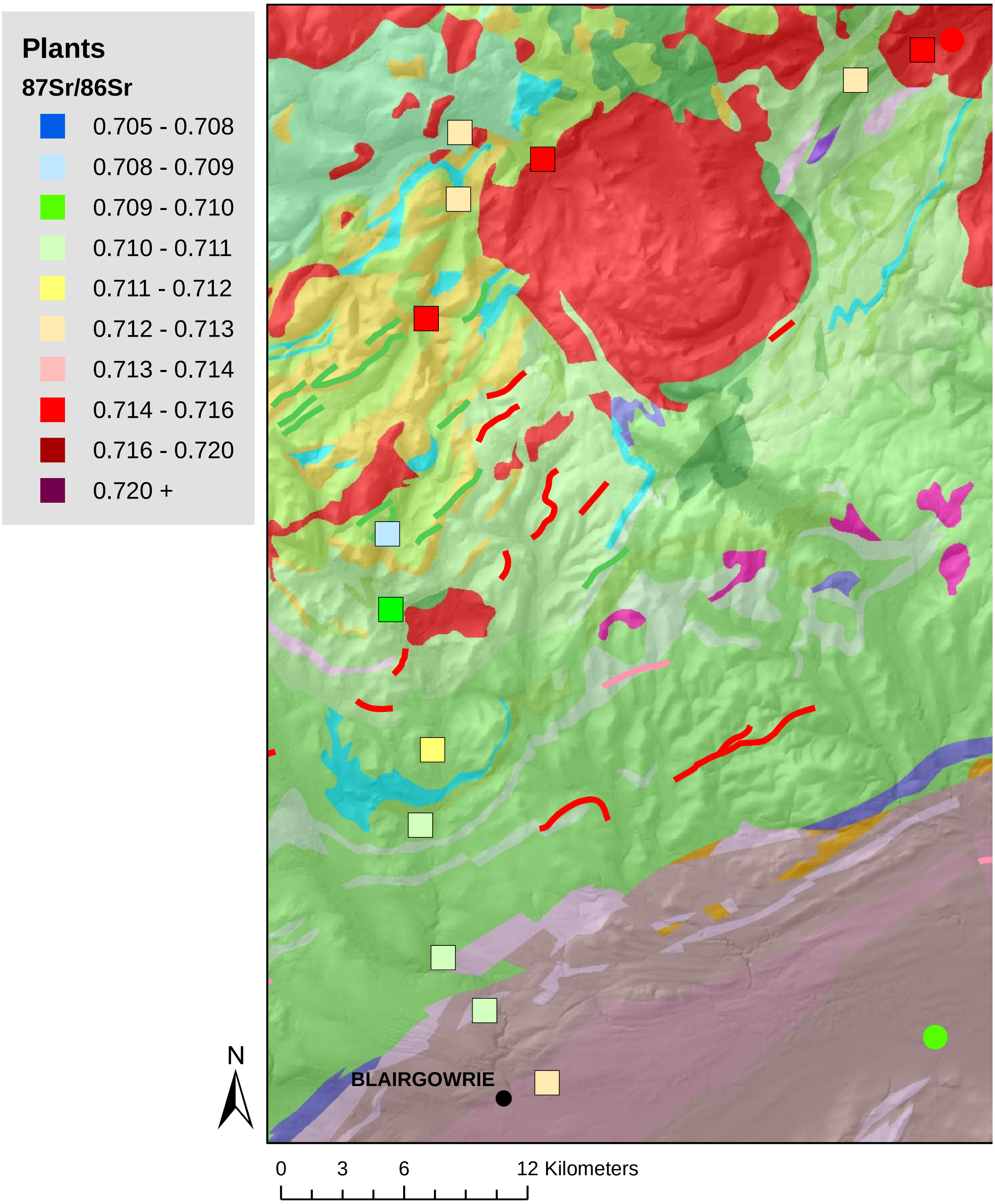
The maximum plant $^{87}Sr/^{86}Sr$ expected in the Cairngorms National Park is currently ~0.718. For water samples in the Cairngorms National Park, higher values >0.718 are recorded by Montgomery *et al.* (2006) and Evans *et al.* (2010) on and around the granitic rocks of Silurian Cairngorms suite, with a current maximum of ~0.720. The mean biosphere $^{87}Sr/^{86}Sr$ for each of the main bedrock lithologies is as follows:

- The Precambrian Dalradian Supergroup Metasediments: 0.7113 ±0.0024 (n=14 , 2SD: Evans *et al.,* 2010; this chapter)
- The Precambrian Dalradian Supergroup Metalimestones: 0.70795 (SCOT L22), 0.70844 (SCOT CTL4) and possibly 0.70879 (SCOT L8)

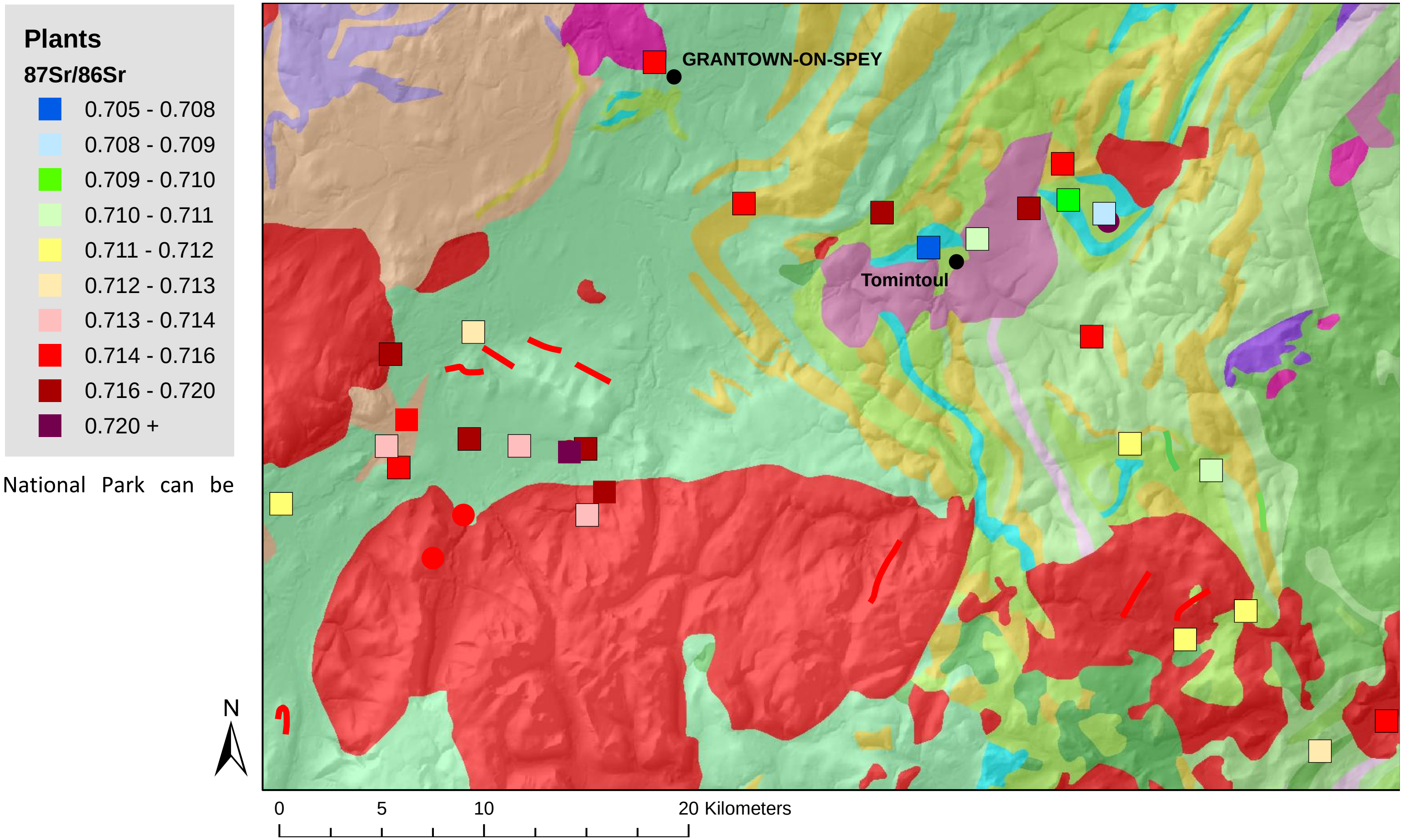
- The Precambrian Dalradian Supergroup Quartzites: 0.7141 ±0.0013 (n=5, 2SD)
- Precambrian Mafic Metamorphic igneous intrusion: 0.71066 (SCOT L4)
- The Ordovician Grantown Pluton: 0.71463 (SCOT L25)
- The Silurian Abergeldie Complex: 0.71064 (SCOT L14)
- The Silurian Cairngorm suite: 0.7155 ±0.0014 (n=8, 2SD: Evans *et al.,* 2010; this chapter).
- The aureole of the Cairngorm and Monadhliath Plutons: 0.7174 ±0.0049 (n=7, 2SD: Evans *et al.,* 2010; this chapter), with one elevated value at 0.72660 (EBP-48: Evans *et al.,* 2010)
- Lower ORS (Blairgowrie): 0.7098 ±0.0010 (n=29, 1SD: Evans *et al.,* 2010), with two elevated values at 0.71267 (SCOT L1) and 0.71100 (SCOT L2).
- Lower ORS outlier (Tomintoul): 0.71094 (SCOT CTL1) and 0.71656 (SCOT CTL2)

5.Figures


GRANTOWN-ON-SPEY
Tomintoul
BLAIRGOWRIE
N
0
5
10
20 Kilometers



Plants
87Sr/86Sr
0.705 - 0.708
0.708 - 0.709
0.709 - 0.710
0.710 - 0.711
0.711 - 0.712
0.712 - 0.713
0.713 - 0.714
0.714 - 0.716
0.716 - 0.720
0.720 +
N
BLAIRGOWRIE
0
3
6
12 Kilometers



National Park can be

Figure 5.1. The plant $^{87}Sr/^{86}Sr$ from across the Cairngorms National Park, alongside GIS data of the 1:625000 Bedrock Geology map (BGS, DiGMapGB, 2007): a. full map of the whole of the Cairngorms National Park; b. first half of the transect from Blairgowrie to Ballater; c. second half of the transect from Ballater to Grantown-on-Spey, as well as the plant $^{87}Sr/^{86}Sr$ from around Chapeltown and between Aviemore and Glenmore. The main legend for the Bedrock geology can be seen in Figure X. Other place names commonly referred to in the Cairngorms seen in Figure 1.3 in chapter 1.

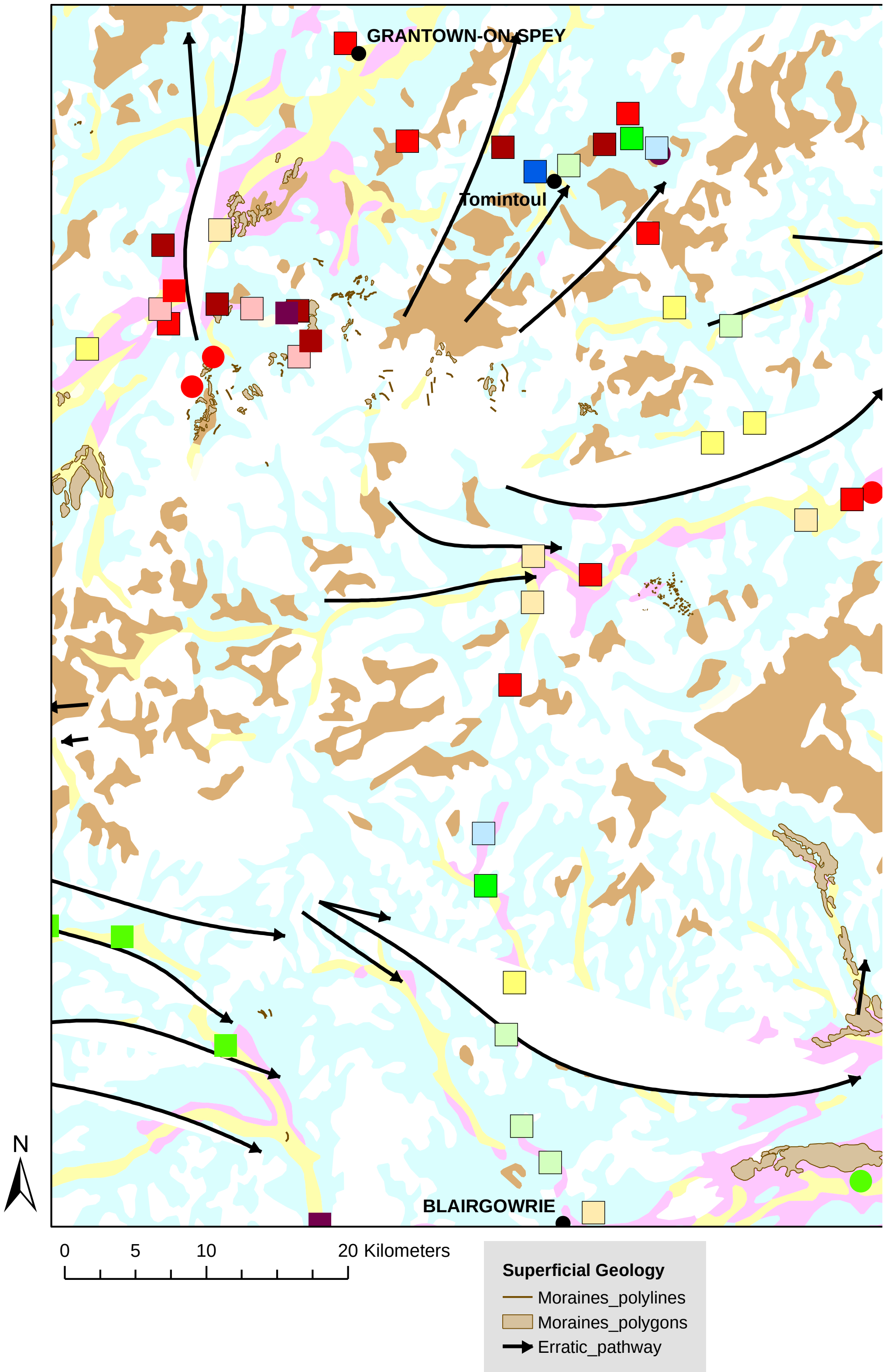


Figure 5.2. The plant $^{87}Sr/^{86}Sr$ from across the Cairngorms National Park in Scotland, alongside GIS data of the 1:625000 Superficial Geology map (BGS, DiGMapGB, 1977) and BRITICE (Clark *et al.*, 2004; 2017). The legend for the Superficial Geology can be seen in Figure X. The plant $^{87}Sr/^{86}Sr$ legend can be viewed in Figure 5.1 above. Other place names commonly referred to in the Cairngorms National Park can be seen in Figure 1.3 in chapter 1.

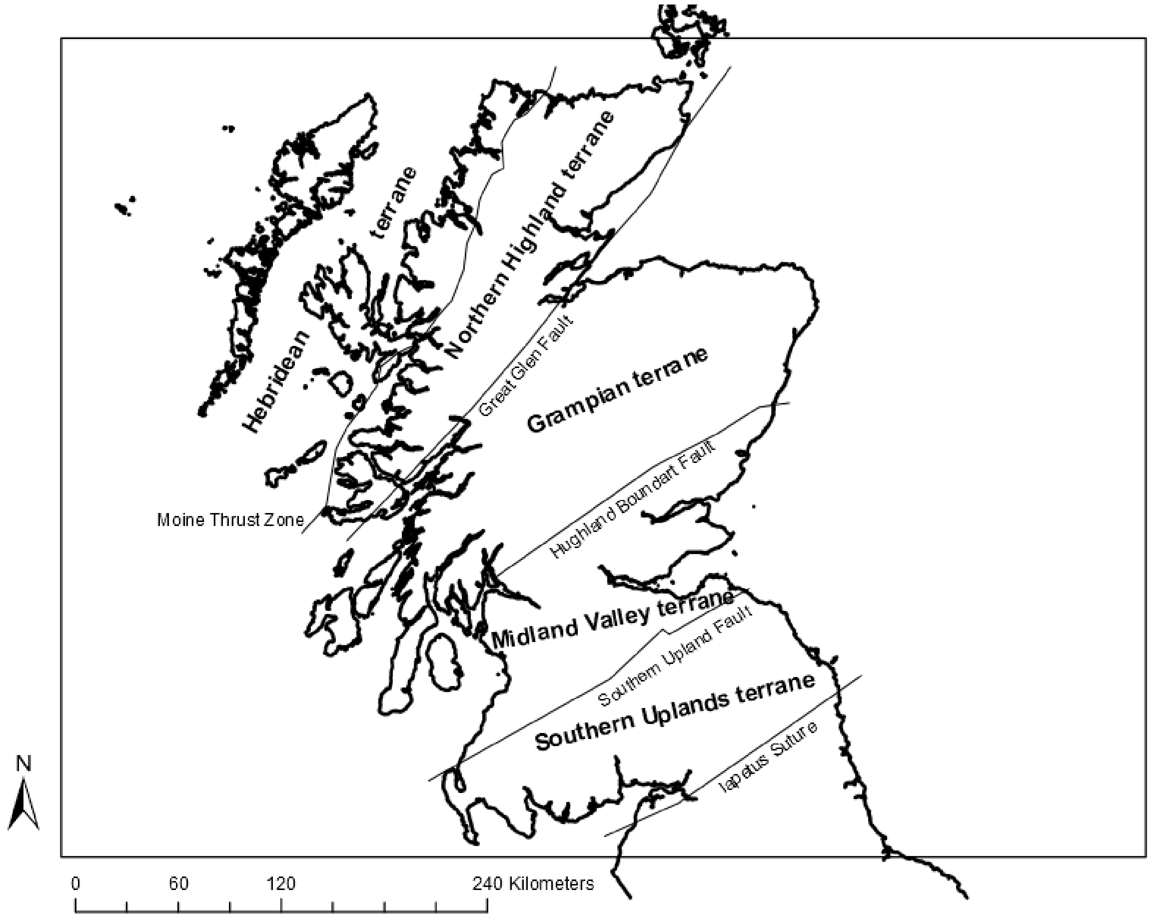


Figure 5.3. The position of the Grampian terrane in comparison to the other terranes in Scotland (based on Figure 1.3 in Trewin & Rollin, 2002, p.2-3).

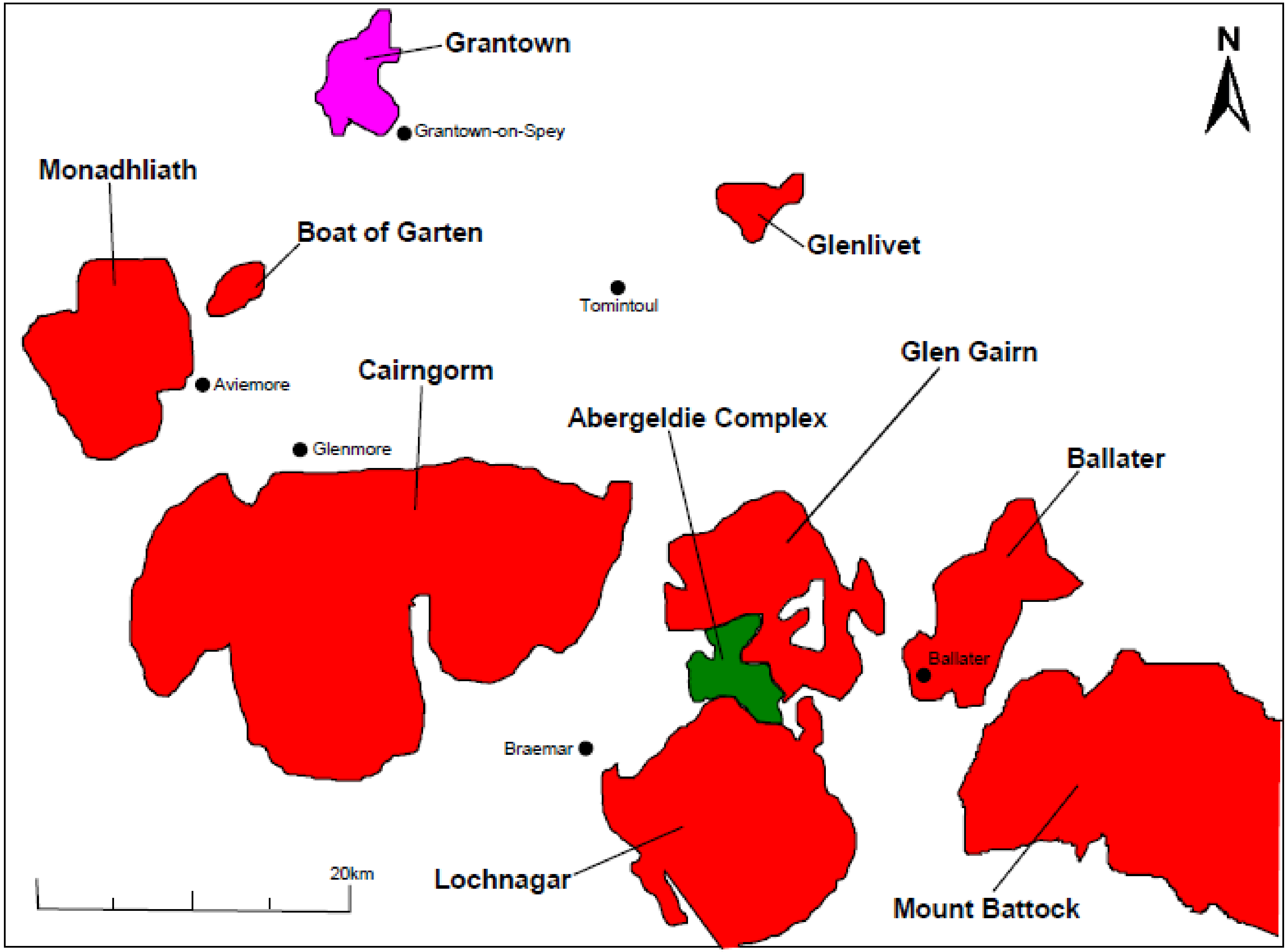
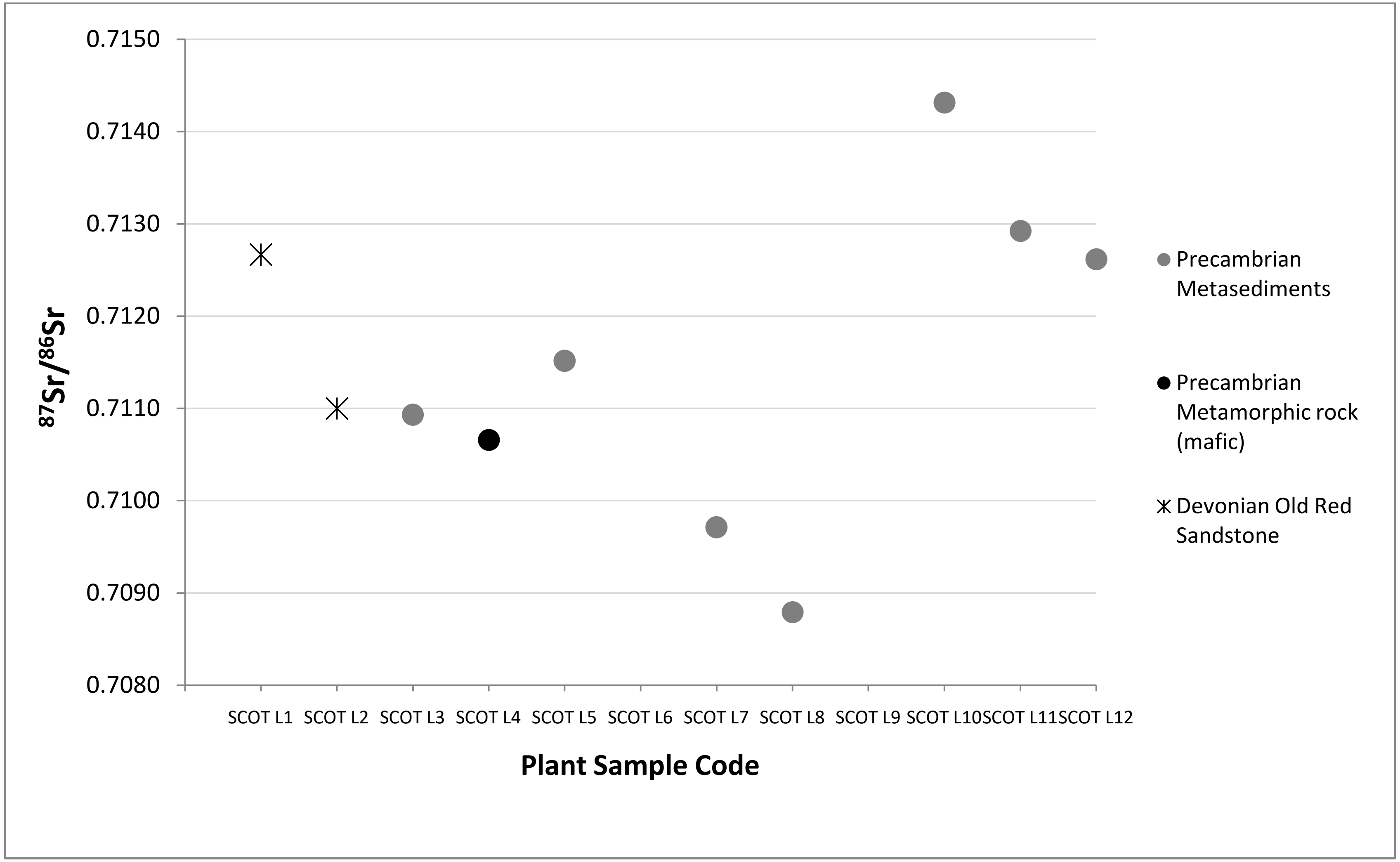


Figure 5.4. The Ordovician Grantown Pluton (pink) and Silurian Cairngorm suite (red) and Abergeldie Complex (green) in the Cairngorms National Park.


0.7150
0.7140
0.7130
0.7120
0.7110
0.7100
0.7090
0.7080
^{87}Sr/^{86}Sr
SCOT L1
SCOT L2
SCOT L3
SCOT L4
SCOT L5
SCOT L6
SCOT L7
SCOT L8
SCOT L9
SCOT L10
SCOT L11
SCOT L12
Plant Sample Code
Precambrian Metasediments
Precambrian Metamorphic rock (mafic)
Devonian Old Red Sandstone

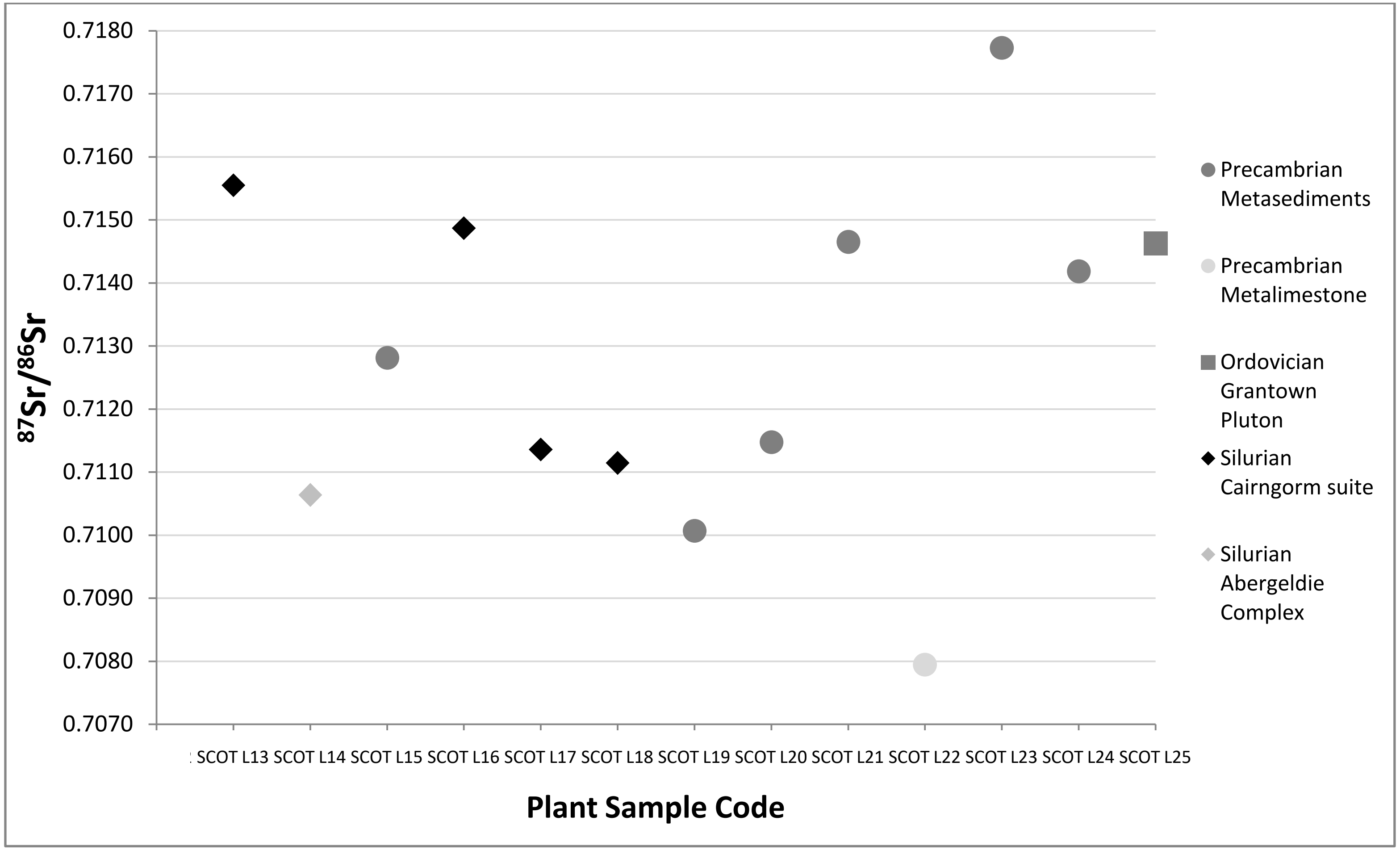


Figure 5.5. The plant $^{87}Sr/^{86}Sr$ collected from across the Blairgowrie to Grantown-on-Spey transect, through the Cairngorms National Park in Scotland, based on the age of the main bedrock geology from which they were taken. The first graph (previous page) contains plant samples SCOT L1 -12, while second graph (this page)contains SCOT L13-25. Plant samples SCOT L6 and SCOT L9 were unsuccessful (see section 5.3)

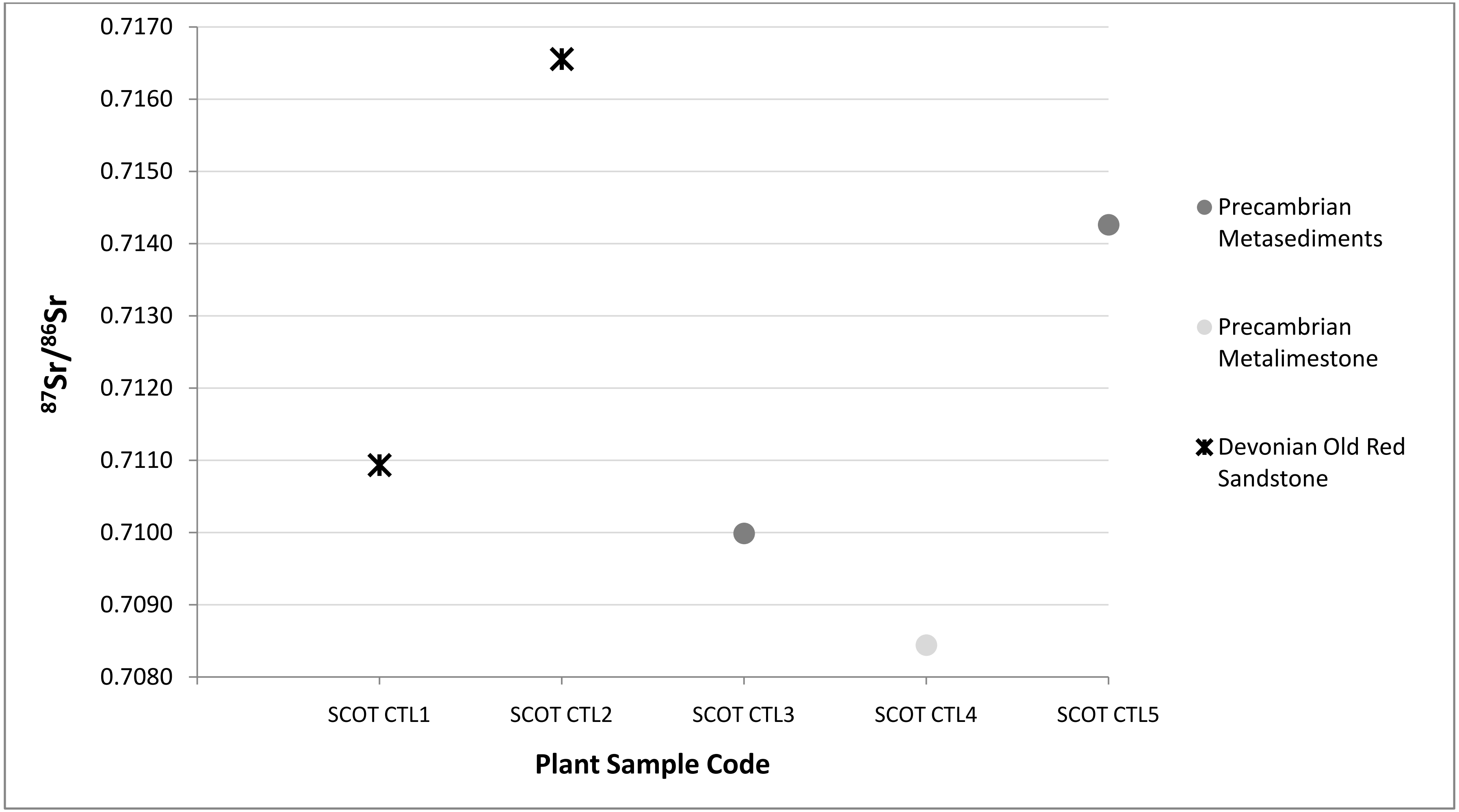


Figure 5.6. The plant $^{87}Sr/^{86}Sr$ collected from around Chapeltown, Moray, Scotland, based on the age of the main bedrock geology from which they were taken.

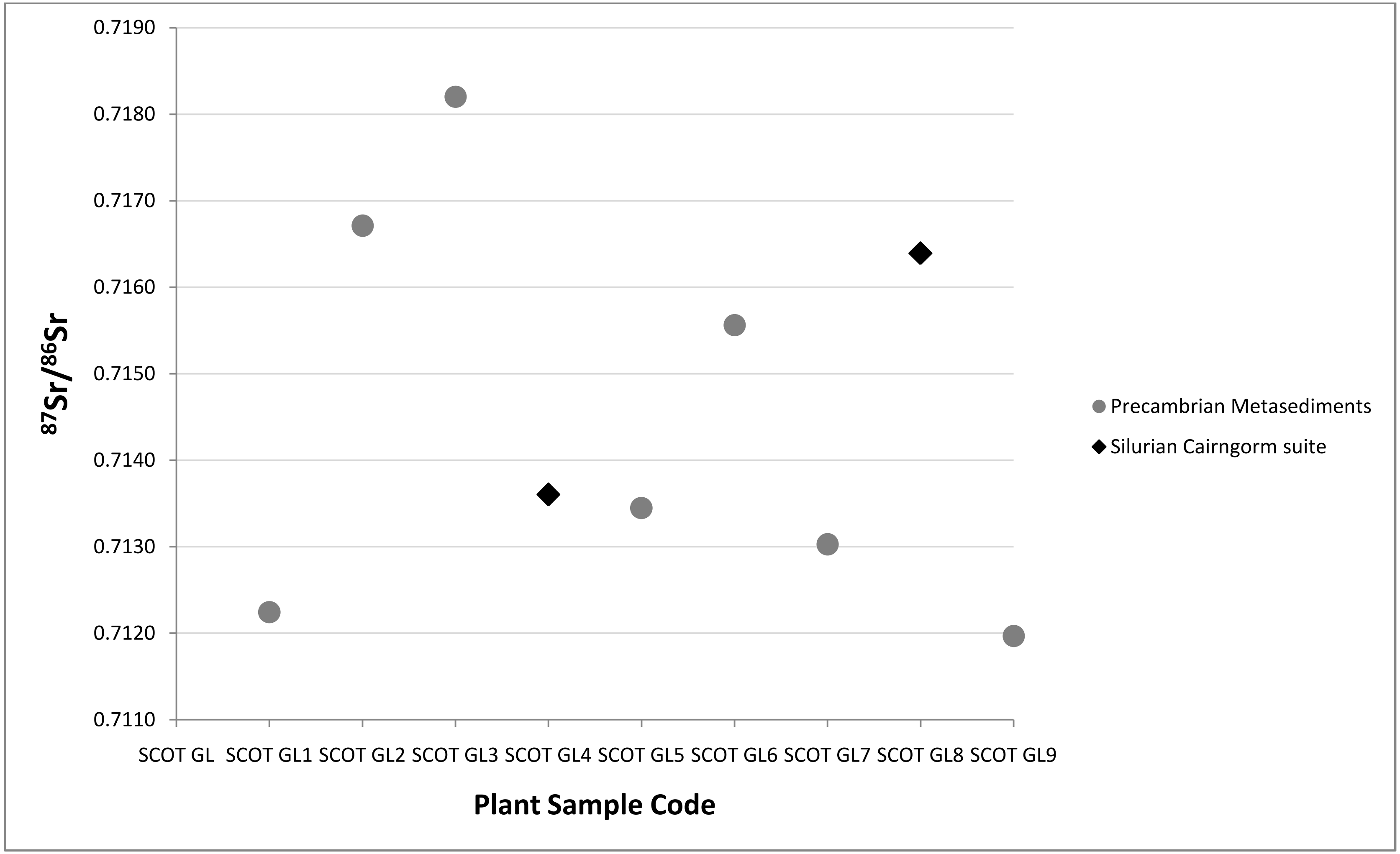


Figure 5.7. The plant $^{87}Sr/^{86}Sr$ collected around Aviemore and Glenmore in the Scottish Highlands, based on the age of the main bedrock geology from which they were taken.

6. The Woodland Effect: plant $^{87}Sr/^{86}Sr$ from forest to farmland.

Aside from trying to define any radiogenic Sr-isotope biospheres through the bedrock geology of Britain, there could be other environmental factors that lead to an unusual or unexpected rise in the $^{87}Sr/^{86}Sr$ of the biosphere in certain areas. Throughout chapter 4 and as will be seen in the following chapter 7, various mixed plant samples have recorded higher values than seen in other biosphere samples also based on the same bedrock lithology. A few of these mixed plant samples are known to have been rooted directly in the exposed bedrock. Their $^{87}Sr/^{86}Sr$ values most likely represents the plants access to any bioavailable Sr from the mineral decomposition of the rock they are rooted in, resulting in a higher value than is obtained when Sr is obtained through the additional medium of soil and soil pore waters. Such cases can be seen in the Lake District (chapter 4, section 4.10.3), and the Forest of Dean (chapter 7, section 7.5.2). For the remaining samples though, the only difference has been that they were collected from woodland. Such cases have been seen in the study areas of Charnwood Forest (chapter 4, section 4.1.4), Nuneaton (chapter 4, section 4.3.3), the Stanner-Hanter Complex (chapter 4, section 4.9.3) and the Lake District (chapter 4, section 4.7.3). The woodland effect may have resulted in their higher $^{87}Sr/^{86}Sr$ values: where the where leaf litter in the woodlands, forming the humus layer, can potentially increase the pH of precipitation as in percolates through soil, leading to the increased leaching of Ca-minerals, and therefore low $^{87}Sr/^{86}Sr$, within the soil though time(chapter 2, section 2.4.3).

In southern England where Mesozoic bedrock dominates, these environmental factors are not expected to lead to any radiogenic $^{87}Sr/^{86}Sr$ values (i.e. >0.714), but perhaps elevate the $^{87}Sr/^{86}Sr$ enough that at most they could define their own small domain, leading to more variability in the local Sr-isotope biosphere. This could therefore alter, to some extent, interpretations of migration and mobility from human and animal $^{87}Sr/^{86}Sr$. The preliminary study in this chapter was designed to distinguish any possible change in the biosphere$^{87}Sr/^{86}Sr$ because of a woodland setting.

6.1. Forests and Woodlands in Britain

Forest and woodlands were extensive in Mesolithic Britain. They ranged in nature from uneven and patchy to continuous closed canopies, but nevertheless they were present throughout Britain (Rackham, 2006, p.60ff; Whitehouse & Smith, 2010).This woodland environment remained until the Mesolithic-Neolithic transition (*ca* 4000 BC), when a strong environmental change was caused by deforestation as humans started to take up agricultural practices during the Neolithic and into the Bronze Age. Many pollen analyses, other environmental proxy studies (such as beetle assemblages)and archaeological evidence show varying stages of deforestation across Britain (Rowley-Conwy, 1982; Darvill, 1987, p.51-54; Greig; Chambers; Birks, 1996; Brown, 1997; Robinson, 2000a; Bell & Walker, 2005, p.164-168; Rackham, 2006, p.60ff, 77ff; Thomas, 2008; Whitehouse & Smith, 2010). It has been estimated that England may have lost 50% of its woodland cover by the Iron Age (Bell & Walker, 2005, p.164-168). From this transition point onwards, agriculture has intensified and expanded into modern times. Nowadays, agriculture accounts for approximately 75% of all the land-use in Britain (Khan *et al.,* 2011).

How much influence deforestation and agricultural practices over the years has had on the Sr-isotope biosphere of Britain is not really known. Evans *et al.* (2010) have provided validation for using modern proxy data to establish biosphere values for the past. This was achieved through the comparability of diagenetically altered bone and dentine values (which should reflect the $^{87}Sr/^{86}Sr$ of the ancient pore fluid at, or shortly after, burial) with modern proxy values, including, significantly, mineral water from Montgomery *et al.*(2006) which by definition must be free of modern pollutants. Whether modern pollutants and fertilisers are changing this validation in certain locations is still debatable (considering Crowley *et al.,* 2015 in chapter 2, section 2.2) and the same might be true for the woodland effect too.

The use of modern fertilisers and their potential $^{87}Sr/^{86}Sr$ inputs have been described in chapter 2, section 2.2. They can supply more or less radiogenic values to the biosphere depending on what fertiliser is used (Vitoria *et al.,* 2004). Sometimes the $^{87}Sr/^{86}Sr$ of fertilisers is undistinguishable from the $^{87}Sr/^{86}Sr$ released into the biosphere from bedrock geology, but when it is significantly different, it may shift the overall $^{87}Sr/^{86}Sr$ of groundwater and rivers towards that of the fertiliser when it is washed out from the soils (Bentley, 2006, p.150-154). It is still debatable how much fertilisers contribute to the overall $^{87}Sr/^{86}Sr$ in the biosphere and transfer through the food-chain. In the past these modern commercial fertilisers were not used, but alternative types of natural fertilisers were: manure was a commonly used fertiliser, being recorded as far back as 6,000 years BC from Neolithic sites across Europe (Bogaard *et al.,* 2013) and the application of seaweed to improve and fertilise soils in island locations also appears to have a long history and a potential impact on biosphere $^{87}Sr/^{86}Sr$ (Kvamme *et al.* 2004; Montgomery *et al.* 2007). The $^{87}Sr/^{86}Sr$ of the manure was likely reflective of the ingested vegetation consumed locally by the animal and it is this value that would have been returned to the soil. The other common fertiliser used from the Roman period onwards was lime (Goulding *et al.,* 1989; Goulding, 2016), with a $^{87}Sr/^{86}Sr$ of ~0.708-0.709. Depending on the bedrock geology underlying the land it was applied to, lime could influence the biosphere $^{87}Sr/^{86}Sr$, but the use of lime on chalk or limestone bedrocks will likely be indistinguishable. The main point here is that humans have been altering the environment for a long time. It is still believed that biosphere $^{87}Sr/^{86}Sr$ from the majority of modern proxies can be inferred into the historical past successfully (Evans *et al.,* 2010). However, the emerging trend of woodland having higher values than unforested, agricultural land on the same bedrock, means that prehistoric archaeological Sr-isotope analysis studies may have to consider this woodland effect in their interpretation, particularly if their study areas were known to have extensive woodland present during their specific time period or were recently deforested.

To compare with modern agricultural land, ancient woodlands are more likely show any change that may have occurred in the Sr-isotope biosphere. By definition, an ancient woodland in Britain has to have been present since 1600 AD (but many are far older, >millennia) and unlikely to have been converted to farmland in the last few centuries. Approximately 2% of Britain is now ancient woodland (Spencer & Kirby, 1992; Forestry Commission England, 2010; The National Trust; The Woodland Trust). These ancient woodlands are more likely to have had the time needed for the woodland effect to accumulate radiogenic values in the biosphere via the depletion of Ca and loss of low $^{87}Sr/^{86}Sr$ values. Deciphering whether ancient woodland and agricultural land, on the same bedrock geology, can have differing $^{87}Sr/^{86}Sr$ could indicate how much influence humans have had on the Sr-isotope biosphere recorded today.

Two study areas were chosen to further test the woodland effect: a larger transect through the Sherwood Forest, Nottinghamshire; and a smaller transect through Burbage

Woods, Leicestershire. Both transects were based entirely on Triassic sedimentary bedrock. Sherwood Forest, or specifically Sherwood Forest National Nature Reserve, covers approximately 4.23 km^2. This areas has been wooded since the early Holocene, after the end of the last glacial period in Britain (~9000 years ago) and was once part of the medieval 40km^2 Royal Forest of Sherwood. This forest is currently home to over a thousand ancient oak trees, with many known to be >500 years old and the most famous being the Major Oak aged between 800-1000 years old (Natural England, 2014; The Sherwood Forest Trust). Heading approximately 70km south of Sherwood Forest is Burbage woods and common in Leicestershire. Altogether the woods and common cover approximately 0.75$km^2$and date back to 1600 AD. Land that is referred to as a 'common' is owned by a person, or people, in which others, known as commoners, may have certain traditional rights such as the right to graze livestock (the right of pasture). In the Medieval period in Britain common land was usually owned by the manorial estates. Burbage common is now owned by the borough council and is now managed as a hay meadow. It is also a site of special scientific interest (BBC, Domesday Reloaded, 1986; Hinckley and Bosworth Borough Council, 2016). Both Sherwood Forest and Burbage woods have modern plantations that were considered during collection of plant samples (the northern most section of Sherwood Forest National Nature Reserve and the Elmesthorpe Plantation at Burbage woods).

6.2. Geological summaries of Sherwood Forest (Nottinghamshire) and Burbage Woods (Leicestershire)

The Triassic sediments that form the majority of the bedrock in the county of Nottinghamshire and approximately half of the bedrock in Leicestershire were deposited in a series of fault-bounded basins when the part of the supercontinent Pangaea, that is now England, was subsiding and breaking apart (Carney, 2010). Sherwood Forest and the remaining transect across the surrounding agricultural land are based on the Sherwood Sandstone Group, which consists mainly of red, yellow and brown sandstones interbedded with conglomerates and are indicative of fluvial origins. These were deposited in the East Midland Shelf, which is linked to the Hinckley Basin (BGS, 1966, Sheet 113; Warrington *et al.,* 1980; BGS, 1998, Sheet 101; Howard *et al.,* 2008). The Quaternary Superficial deposits over the Sherwood Forest area are sporadic, mainly consisting of alluvium with some larger glacial till deposits and river terrace deposits found further north heading towards the village of Blyth in Nottinghamshire (BGS, 1966, Sheet 113; BGS, 1998, Sheet 101).

Burbage woods is based on the Triassic Mercia Mudstone Group, which was deposited in the Hinckley Basin, which overlies the Sherwood Sandstone Group described above (Warrington *et al.,* 1980; BGS, 1994, Sheet 169; Bridge *et al.,* 1998, p.87; Howard *et al.,*2008). This group is comprised of formations that are argillaceous in nature (containing lots of clay minerals) being dominated by red mudstones which are often referred to as 'red beds', but also contain subordinate siltstones with thick halite-bearing units in some basinal areas. The majority of the 'red beds' are thought to be deposited through wind action in subaqueous playas or inland sabkha environments (Warrington *et al.*, 1980; Bridge *et al.,* 1998, p.87, 92-95; Carney, 2010). The Mercia Mudstone Group is poorly exposed (Bridge *et al.,* 1998, p.92) being covered by a variety of Quaternary Superficial deposit. Much of the north, in and around the village of Burbage is covered by the Thrussington Till and Wolston Clay of the Wolston Glacial Succession (deposited in the Anglian). Travelling further south the variety of Superficial deposits widens including much of the Wolston Glacial Succession with possible post-glacial deposits like the Dunsmore Gravel and small areas of peat (BGS, 1994, Sheet 169; Bridge *et al.,* 1998, p.98-117).

The $^{87}Sr/^{86}Sr$ expected from the biosphere on these Triassic bedrocks is 0.7097 ±0.0006 (n=54, 1SD, mainly water samples; Evans *et al.,* 2010). However, mixed plant samples on Triassic bedrock within chapter 4 have shown to produce more radiogenic values between 0.710-0.712 (see Charnwood Forest, section 4.1, the Malvern Hills, section 4.2 and Nuneaton, section 4.3).

6.3. Geochemical Survey and Field-notes for Sherwood Forest and Burbage Woods

In July 2016, a total of eight locations were visited across a transect that stretched from around Farnsfield, up through Sherwood Forest National Nature Reserve and towards Blyth (Nottinghamshire). The weather over the collection period was sunny and dry. In August 2016, a total of six location were visited across a smaller transect that ran from Burbage woods and common (Leicestershire) through to the village Pailton (Warwickshire). The weather over the collection period was sunny and humid, but no rain occurred. The three plants collected from each location in both transects were mixed by the methods described in chapter 3, section 3.2. No plants were directly taken from the agricultural fields, e.g. no crops, etc., were sampled. Only the plants from the tree verges and open land surrounding such fields were collected and plant $^{87}Sr/^{86}Sr$ data from these samples are referred to heron in as 'on agricultural land', as they are expected to still be influenced by agricultural practices. The field-notes for the mixed plant samples from across Sherwood Forest and Burbage Woods can be viewed in Appendix 2. These mixed plant samples then followed the same methods for chemical preparation and Sr-isotope analysis outlined in section 3.3 in chapter 3.

6.4. Plant $^{87}Sr/^{86}Sr$ Results

6.4.1. Sherwood Forest

The plant $^{87}Sr/^{86}Sr$ from across the Sherwood Forest transect can be seen in Figure 6.1, while Figure 6.2 displays the locations of plant $^{87}Sr/^{86}Sr$ alongside the bedrock geology and Quaternary superficial deposits. The plant $^{87}Sr/^{86}Sr$ collected from the Sherwood Forest Nature Reserve have the highest values at 0.71358 (SF L1) and 0.71757 (SF L3). The sample SF L2, also collected from Sherwood Forest, was unsuccessful in its first and second repeated runs for Sr isotope analysis by TIMS at the NIGL (Keyworth). Although there are only two results from Sherwood Forest Nature Reserve currently, SF L3, at

0.71757, is higher than expected. It has a difference of approximately +0.004 compared to the other woodland sample, SF L1. No concerns were raised during the analysis on the TIMS at the NIGL (Keyworth) and no peculiarities were noted in the field-notes of this sample, apart from that long horn cattle were allowed to graze in this part of the forest (Appendix 2). As all the oak foliage was collected from a height inaccessible to these cattle, so contamination from them was considered low. It would be very interesting to see if further samples from the ancient woodlands of Sherwood Forest can reproduce such high $^{87}Sr/^{86}Sr$ as seen by SF L3.

As for the mixed plant samples taken from around agricultural land, SF L4 is elevated, at 0.71218, compared to the other plant $^{87}Sr/^{86}Sr$ = 0.7098 ±0.0008 (n=4, 2SD). SF L4 is the nearest sample taken from around agricultural land to the Sherwood Forest Nature Reserve, being approximately 2km south of the forest (Figure 6.2). It is also approximately 1km north of the Sherwood Pines Forest Park, which covers an area of approximately 13.4km^2 (The Forestry Commission England, 2017). The majority of the medieval 40km^2 Royal Forest of Sherwood has only been lost in the last 230 years (Natural England, 2014; The Sherwood Forest Trust) and it is possible the surrounding land around the current Sherwood Forest Nature Reserve was deforested more recently. Sherwood Pines Forest Park is managed for timber by the Forestry Commission England (2017), so none of the trees in Forest Park are as old as the ones in Sherwood Forest Nature Reserve, but the area has been wooded since the time of the medieval Royal Forest of Sherwood (The Sherwood Forest Trust). Therefore, it is proposed that the sample SF L4 still shows some influence from these woodlands. All the remaining plant $^{87}Sr/^{86}Sr$ based around agricultural land are at least 4km away from any of the forests or woodlands of Sherwood and have plant $^{87}Sr/^{86}Sr$ between 0.70932 -0.71028. If SF L4 is considered a woodland sample *sensu lato,* then the woodlands on the Sherwood Sandstone Group have a significant difference of approximately +0.002 minimum compared to the highest plant $^{87}Sr/^{86}Sr$ on agricultural land.

6.4.2. Burbage Woods

The plant $^{87}Sr/^{86}Sr$ from across the Burbage woods transect can be seen in Figure 6.3, while Figure 6.4 displays the location of plant $^{87}Sr/^{86}Sr$ alongside the bedrock geology and

Quaternary superficial deposits. The sample BW L1 from Burbage woods has the highest value at 0.71243, while the lowest value at 0.71019 (BW L5) is from around agricultural land. The common is currently managed as a hay meadow and so should be seen as agricultural land.

Figure 6.4 also displays the plant $^{87}Sr/^{86}Sr$ from the study area of Nuneaton (chapter 4, section 4.3), in which the mixed plant samples NUN L1 (0.71110) from Burbage woods and NUN L2 (0.71140) from around agricultural land, are still on the Triassic Mercia Mudstone Group. Also there are the plant samples CHW 17 (0.71219), CHW 18 (0.71209), CHW 19 (0.71142: chapter 4, section 4.1) from Swithland woods in Charnwood Forest, that are also based on the Mercia Mudstone Group in the Hinckley Basin. If these samples from the Mercia mudstone Group from the Charnwood Forest and Nuneaton study areas are also included, then the woodlands on the Mercia Mudstone Group have plant $^{87}Sr/^{86}Sr$ = 0.7119 ±0.0010 (n=6, 2SD), while the agricultural land (including Burbage common) have plant $^{87}Sr/^{86}Sr$ = 0.7113 ±0.0015 (n=5, 2SD). The difference between the mean plant $^{87}Sr/^{86}Sr$ of the woodlands and the agricultural land is +0.00057 approximately, which is not a significant change in the $^{87}Sr/^{86}Sr$ (significant being ±0.001 or greater: chapter 2, section 2.2). Also the majority of the woodland values fall within 2SD of the agricultural land values and therefore there are no distinguishable trends.

Burbage woods is small in size, <1km^{2}and approximately 400 years old(this is similar for Swithland Woods in Charnwood Forest). It could be possible that the woodland is not large or old enough to cause any change in the biosphere on the Triassic Mercia Mudstone Group. Altogether, the plant $^{87}Sr/^{86}Sr$ = 0.7116 ±0.0013 (n=11,2SD) on Mercia Mudstone Group in the Hinckley Basin and currently shows the bedrock's heterogeneous nature.

6.5. Discussion of plant $^{87}Sr/^{86}Sr$ of Sherwood Forest and Burbage Woods

In Evans *et al.* (2010) the biosphere $^{87}Sr/^{86}Sr$ = 0.7097 ±0.0006 (n=54, 1SD) for Triassic bedrock in Britain. Chenery *et al.* (2011) report further plant $^{87}Sr/^{86}Sr$ data on Triassic bedrock of the East Midlands Shelf, up in north Yorkshire. The Sherwood Sandstone

Group in this area have plant $^{87}Sr/^{86}Sr$ = 0.7096 ±0.0017 (n=5, 2SD). The plant $^{87}Sr/^{86}Sr$in this chapter taken from agricultural land on the Triassic Sherwood Sandstone Group, with 0.7098 ±0.0008 (n=4, 2SD; section 6.4.1), compare well with this previous Triassic data. However, the plant $^{87}Sr/^{86}Sr$ from the ancient woodland of Sherwood Forest (SF L1, SF L3 and SF L4) are higher in value. Combining the plant $^{87}Sr/^{86}Sr$ taken from agricultural land on the Sherwood Sandstone Group of the East Midlands Shelf produces a mean of 0.7096 ±0.0012 (n=10, 2SD: Evans *et al.,* 2010; Chenery *et al.,* 2011; section 6.4.1). There is a difference of approximately +0.0025 minimum between the woodland plant $^{87}Sr/^{86}Sr$ and the agricultural plant $^{87}Sr/^{86}Sr$ on the same Triassic bedrock. This difference is believed to be caused by the woodland effect. Further woodland values would be needed to determine if the woodland effect is reproducible, as only two of the three values are truly based on the ancient woodlands of Sherwood Forest at present (see section 6.4.1).

As for the plant $^{87}Sr/^{86}Sr$ on the Mercia Mudstone Group in the Hinckley Basin (section 6.4.2), only one sample, at 0.71019 (BW L5) falls within the biosphere range reported for Triassic bedrock in Evans *et al.,* (2010). The rest of the plant $^{87}Sr/^{86}Sr$ values are approximately 0.711 or greater, regardless of whether they are based on agricultural land or woodland. Together, they have plant $^{87}Sr/^{86}Sr$ = 0.7116 ±0.0013 (n=11, 2SD). These values are more similar to the plant $^{87}Sr/^{86}Sr$ reported for the Triassic Mercia Mudstone Group near the Malvern Hills, at 0.7114 ±0.0011 (n=7, 2SD: Chenery *et al.,* 2010; chapter 4, section 4.2*)*. Unlike the woodland values on the Sherwood Sandstone Group, the woodland values on the Mercia Mudstone Group are currently indistinguishable from those on agricultural land. Burbage woods and Swithland Woods (in Charnwood Forest) are small in size compared to the Sherwood Forest Nature Reserve and they are also not as old, both being approximately 400 years old compared to 9000 years old Sherwood Forest (section 6.1). The woodland effect in this case is likely negligible on the biosphere. Instead the plant $^{87}Sr/^{86}Sr$ may just reflect the overall heterogeneous nature of the Mercia Mudstone Group bedrock, particularly as similar values are seen near the Malvern Hills on the same bedrock, which were not specifically taken from woodland environments.

There is one more case where the woodland effect can be defined in this thesis currently: the Silurian Ludlow sedimentary bedrock along the Welsh Border. These Silurian rocks have woodland plant $^{87}Sr/^{86}Sr$ at 0.71550 (USK-04: Evans, *pers.com*) and 0.71613 (SHC L5: chapter 4, section 4.6), while the plants from around agricultural land have $^{87}Sr/^{86}Sr$ = 0.7122 ±0.0029 (n=4, 2SD: Evans, *pers.com*.; chapter 4, section 4.6). This is a difference of approximately +0.002 between the lowest woodland value (USK-04) and highest agricultural value, USK-02 at 0.713334 (Evans, *pers.com*.).Interestingly the mixed plant sample SHC L5, with the highest $^{87}Sr/^{86}Sr$ value, comes from woodland on the outskirts of what was once also a medieval royal hunting forest, known as Radnor Forest. No historical records exist to confirm if it was ever a forest in the modern sense of the word (e.g. a large, densely wooded area), but several woodlands were present since at least 1461 AD, and, along with newer plantations, still exist today. Together they cover approximately 14km^2 (The Forestry Commission, North Wales, 1924-1951; Owen, 1992; AWI, Wales, 2011). The plant sample USK-04 is also taken from ancient woodland believed to be at least 400 years old and covers an area of approximately 2.5km^2 (AWI, Wales, 2011).

As this study is preliminary, further sampling and testing of the woodland effect is needed. From the results in this study, it seems only the larger ancient woodlands (e.g. >1km^2) can cause a significant change of approximately +0.002 in the Sr-isotope biosphere on the Silurian Ludlow sedimentary rocks and Triassic Sherwood Sandstone Group in England and Wales. Unfortunately, trying to observe the same trends for the mixed plant samples collected from the Cairngorms National Park in Scotland (chapter 5) was not possible, as the majority of these samples were collected from woodland and had no agricultural comparatives on the same geological bedrock. Therefore, it is possible that the samples collected from across the Cairngorms National Park have higher $^{87}Sr/^{86}Sr$ because of the woodland effect. If this trend can be repeated in other ancient woodlands in Britain on a variety of different bedrocks, it will affect interpretations of archaeological human and animals $^{87}Sr/^{86}Sr$, particularly those from prehistory.

If any areas were known to be extensive woodlands in a particular time period but are now agricultural land, then the $^{87}Sr/^{86}Sr$ recorded in the biosphere can be predicted to be higher. How much higher still needs to be defined and will likely change depending on the particular lithology and mineralogy of the bedrock geology, however there are certain animals and humans for which this woodland effect will have major implications. For example, the grazing of domesticated animals (cattle and pigs) in forests is believed to have occurred since the Neolithic (Rowley-Conwy, 1987; Brown, 1997; Robinson, 2000a,b) as well as the feeding of leaf fodder to stalled animals (Bell & Walker, 2005, p.164-168). For these animals their $^{87}Sr/^{86}Sr$ should naturally be expected to be higher than recorded by modern plant samples if they have been collected from around agricultural land. The importance of woodlands may also be seen in the $^{87}Sr/^{86}Sr$ of Neolithic people in Britain, particularly if the relationships between foragers and farmers in the Neolithic is being challenged. If farmers were indeed clients of the foragers, wanting and even dependent on forager technology and forest products for the first 1500 years of occupation (Robinson, 2000b; Rowley-Conwy, 2014), then this may be seen in their $^{87}Sr/^{86}Sr$, which will likely fall on a mixing line between the $^{87}Sr/^{86}Sr$ of woodlands and the $^{87}Sr/^{86}Sr$ of the land they farm. There then may be a change in human $^{87}Sr/^{86}Sr$ once agricultural practice becomes their dominant source of plants and they no longer rely on plants from the forests or woodlands (with plants being the dominant dietary Sr in human and animals: Burton & Wright, 1995; Montgomery, 2010).

6.6. Concluding remarks

This study has preliminarily shown that large (>1km^2) ancient woodlands in England and Wales can produce more radiogenic $^{87}Sr/^{86}Sr$ by approximately +0.002. These results are still speculative, but if woodlands can alter their own biosphere through the woodland effect they should be seen as a separate domain compared to other plant samples taken from around agricultural land, open grass land, heath land, moor land etc. Further work is needed to confirm if this trend is consistent and to define the change in $^{87}Sr/^{86}Sr$, which likely will change depending on the bedrock geology. Broader sampling of Sherwood Forest would be advantageous to conclude if these results are reproducible and consistent. The addition of Sr-isotope analysis of any local archaeological fauna samples, if available, would be also good for comparison. Wild fauna and domesticated fauna that could have grazed in the woodlands, such as pigs and cattle, would provide an indication if high $^{87}Sr/^{86}Sr$ in woodlands were attainable further up the food-chain. It is still assumed that any areas of open grass land, moor or heath land, etc., have the same biosphere $^{87}Sr/^{86}Sr$ in the past as they record today. It is only areas that heavily forested that may have potentially had a change in their biosphere $^{87}Sr/^{86}Sr$.

The plant $^{87}Sr/^{86}Sr$ based on Triassic bedrock is as follows:

- The East Midlands Shelf, Sherwood Sandstone Group, Agricultural Land: 0.7098 ±0.00082 (n=4, 2SD).

- The East Midlands Shelf, Sherwood Sandstone Group, Sherwood Forest: 0.71218 (SF L4), 0.71358 (SF L1) and 0.71757 (SF L3)

- The Hinckley Basin, Mercia Mudstone Group: $^{87}Sr/^{86}Sr$ = 0.7116 ±0.0013 (n=11, 2SD)

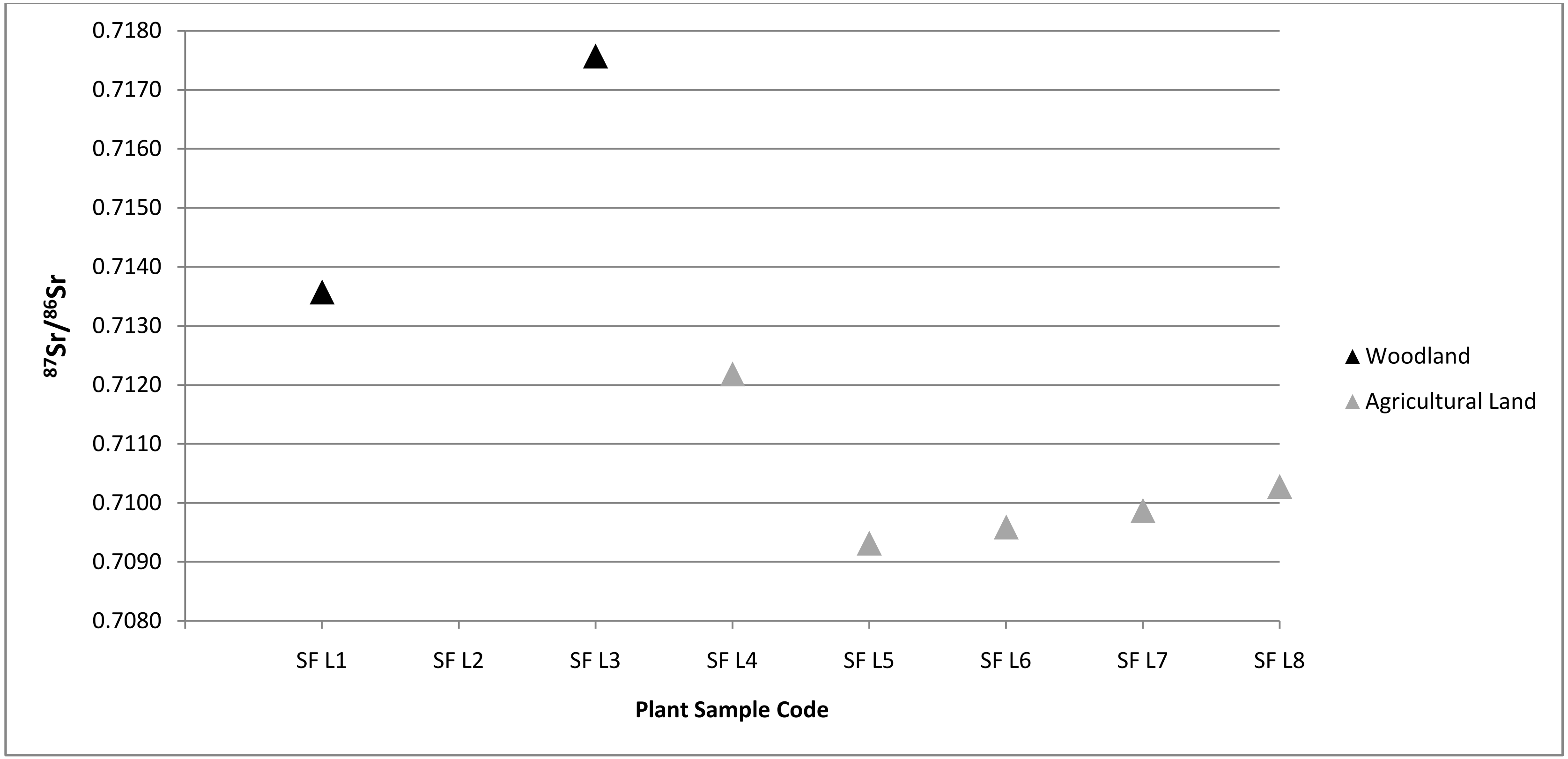


Figure 6.1. The plant $^{87}Sr/^{86}Sr$ from across the Sherwood Forest Transect, on the Triassic Sherwood Sandstone Group. Based on if the plant samples were collected from woodland or from around agricultural land.

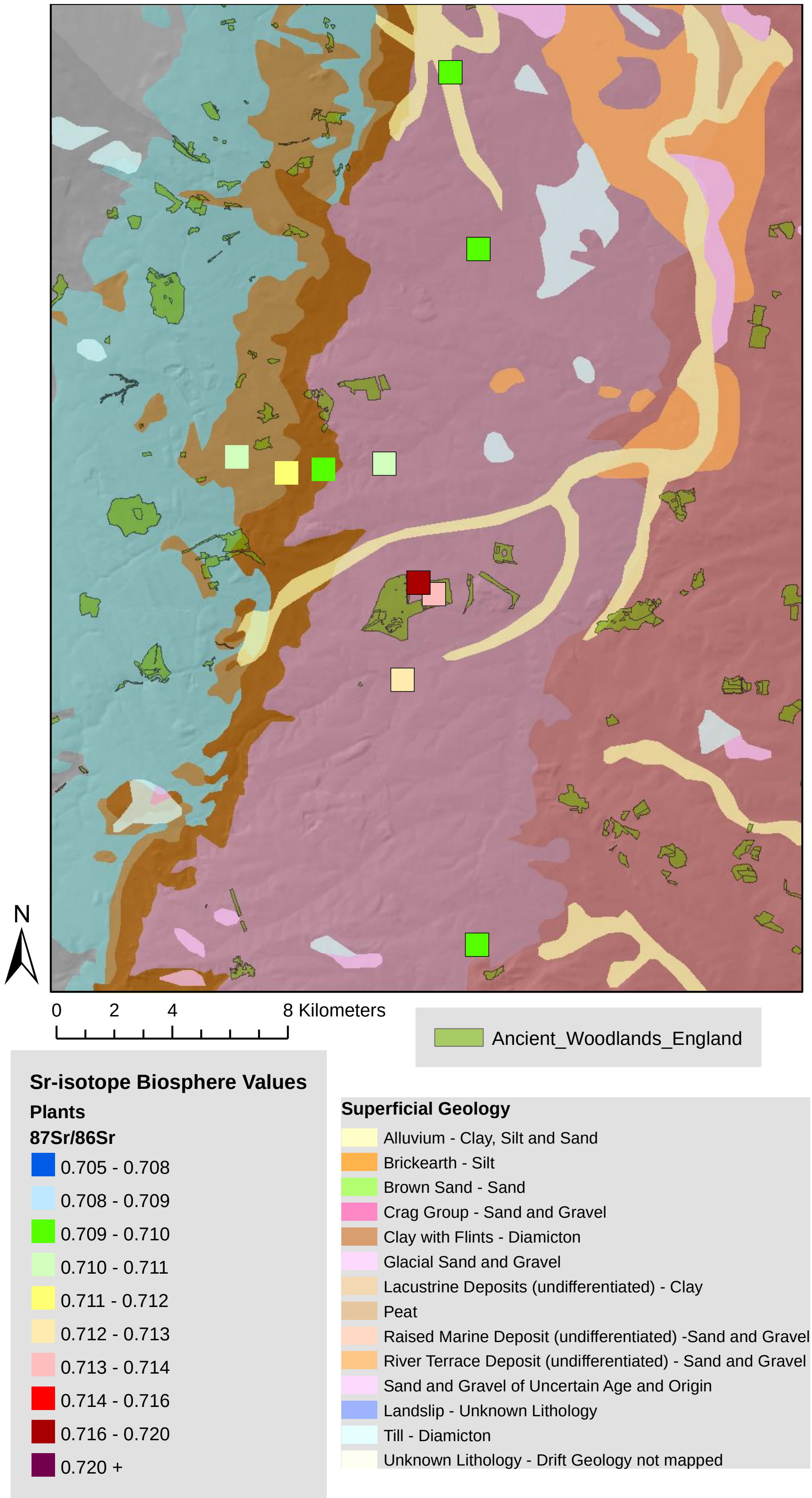


Figure 6.2. The plant $^{87}Sr/^{86}Sr$ from across the Sherwood Forest transect (outlined boxes), along with GIS data of the 1:625000 Bedrock and Superficial Geology maps (BGS, DiGMapGB, 2007; 1977) and Ancient Woodland Inventory, England (AWI, 2013). The legend for all of the Bedrock Geology can be seen in Figure X. The other plant $^{87}Sr/^{86}Sr$ data (not outlined) belongs to NIGL (unpublished).

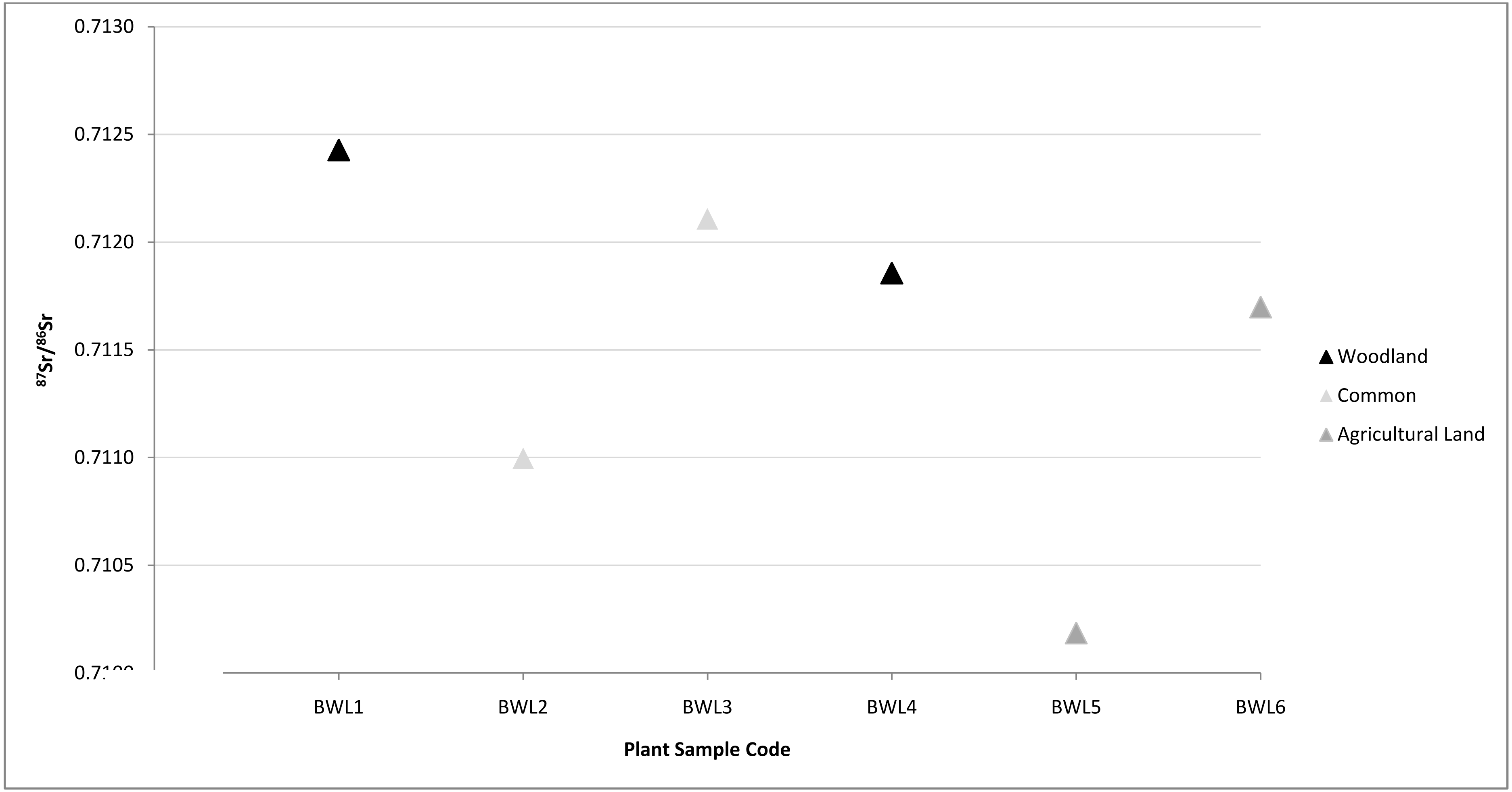


Figure 6.3. The plant $^{87}Sr/^{86}Sr$ from across the Burbage Wood Transect, on the Triassic Mercia Mudstone Group. Based on if the plant samples were collected from woodland or from around agricultural land (common is a type of agricultural land).

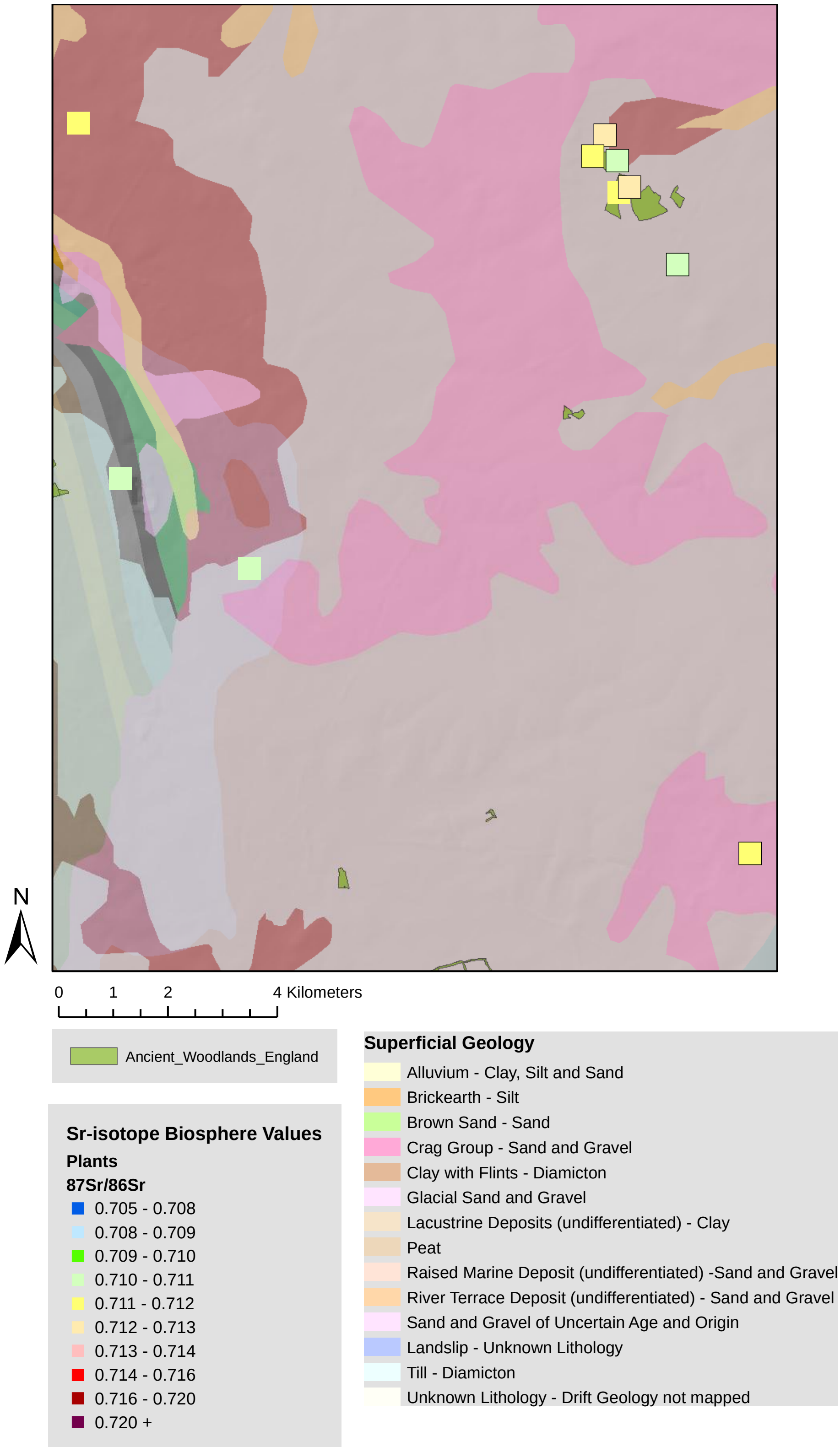


Figure 6.4. The plant $^{87}Sr/^{86}Sr$ from across the Burbage woods and common transect (outlined boxes), along with GIS data of the 1:625000 Bedrock and Superficial Geology maps (BGS, DiGMapGB, 2007; 1977) and Ancient Woodland Inventory, England (AWI, 2013). The legend for all of the Bedrock Geology can be seen in Figure X. The other plant $^{87}Sr/^{86}Sr$ data (not outlined) is from the Nuneaton study area (chapter 4, section 4.3).

7. Contribution of strontium to the human diet from querns and millstones: an experiment in digestive Sr-isotope uptake.

*An edited version of this chapter has been prepared for publication, the authors include Lucie Johnson, Janet Montgomery (Durham University), Jane Evans and Elliot Hamilton (NIGL, BGS). The publication has been dedicated to the late Professor David Peacock, a leading authority and author of 'The Stone of Life. Querns, Mills and Flour Production in Europe up to c.AD 500', whose advice and interest was greatly appreciated in the early stages of the study. Thanks also goes towards Adrian Wood for his assistance during preparing the rocks in the Mineral Separation Laboratory facility at the NIGL (BGS, Keyworth), as well as Mandy Jay for her constructive comments. This study was funded through NIGSFC grant No.IP-1456-0514 awarded to Janet Montgomery. Lucie Johnson is supported by a NERC doctoral studentship (Award Reference No.*1345819*).*

Information about the materials and methods used for the rock and mineral samples are all contained within this chapter. For the plant samples collected from the Forest of Dean the same geochemical survey and methodology for Sr-isotope analysis as in Chapter 3 were followed.

The question of whether rock grit ingested unintentionally from querns or millstones or deliberately through pica or geophagy is bioaccessible in the human gut has not been addressed in archaeological Sr-isotope studies (refer back to Chapter 2, section 2.5). Åberg *et al.* (1998, p.116) has mentioned a similar scenario previously, in that grit from the milling process may have been a major contributor to human $^{87}Sr/^{86}Sr$ values, particularly during the Medieval period. It is also widely recognised that tooth wear in archaeological populations was often far greater than today – one of the main reasons for this is believed to be the coarser diet and particularly the presence of soil and rock in their food, included either accidentally via dirt or grit from grinding, or intentionally as a result of geophagy or pica (Eshed *et al.*, 2006; Deter, 2009).

The study in this chapter addresses the possible contribution that rocks used to grind grain might have made to the $^{87}Sr/^{86}Sr$ obtained through the human diet in the past, from both locally derived and imported grinding materials. It is the first of its kind to employ the use of the Unified Bioaccessibility Method (UBM: Hamilton *et al.,* 2015) for Sr-isotopes from rock grit. Further details of the UBM can be found in section 7.2 and 7.3.3. Alongside the UBM, a series of separate experiments were conducted in the clean lab facilities at the NIGL (BGS, Keyworth) and these can be found in Appendix 4. They mimicked the UBM, but on a smaller scale, and were used to validate the results .

7.1. The nature and type of rocks used for grinding grain

Rocks have been used as tools to grind grain in Britain since the start of the Neolithic in the 4th millennium BC (Peacock, 2013, p.17-21; Watts, 2014, p.19). These grinding tools can be categorized into two main forms: querns, which are hand operated devices usually less than 50 cm in diameter, and millstones which developed later and were often larger (>60 cm in diameter) and much heavier so that hand turning was not always feasible (Peacock, 2013, p.3), necessitating the additional help of wind, water, slave or animal power. Both forms can grind grain to make flour but their production rates vary depending on the type of quern or millstone being used, its lithology, its size and the type of grain being ground. In an assessment of flour production experiments Peacock (2013, p.126-128) concluded that approximately 0.5-4 kg of flour per hour can be produced from a quern (Destexter-Jamotte, 1951; Hennig, 1966; Hampl, 1976; Fröhlich & Waldhauser, 1989; Beranova, 1993; Menasanch, Risch & Soldevilla, 2002; Samuel, 2009). A set of millstones on the other hand can produce approximately 10-50 kg of flour per hour (Peacock, 2013, p.128-129).

The important attribute of a quern or millstone for this study is its lithology, as it is the rock tool itself that contaminates the food that humans digest. Grinding stones of many lithologies have been archaeologically documented in Britain including granite, gneiss, mica schist, gabbro, basalt, sandstone, conglomerate, greensand, silicified limestone, quartzite and andesite (Peacock, 2013, p.62-65; Watts, 2014, p.29-30). Some of these rocks, such as gabbro and basalt, will give low whole rock $^{87}Sr/^{86}Sr$ typically between 0.704 and 0.708, whereas granites and schists can give very high whole rock $^{87}Sr/^{86}Sr$ values, sometimes above 1.0 (Faure & Powell, 1972; Rundle, 1979; Peterman & Hildreth, 1978; Faure, 1986). Granites and gabbros (including their finer crystal grained equivalents such as rhyolites and basalts) represent the extremes of isotope composition, but they were not commonly used in Britain with the possible exception of the imported Mayen Lava from Germany. Instead, the native abrasive sandstones and gritstones were particularly prized and, hence, more commonly used across all periods in Britain (Peacock, 2013, p.2-3, 62-65, 151-154). All the lithologies used in this study are of British origin: Millstone Grit from the Peak District; Pennant sandstone from the Forest of Dean, near the southern borders of Wales; and Eskdale granite from the Lake District, Cumbria (see

Figure 7.1).Certain minerals within the rock that could be separated during grinding were also important. Micas, such as biotite and muscovite, are silicate minerals present in a wide range of igneous, metamorphic and sedimentary rocks. They have a flaky texture and can easily plucked from the rock surface during weathering and kinetic processes such as grinding. Micas commonly have $^{87}Sr/^{86}Sr$ >1.0 (Clauer, 1981; Hampton & Taylor, 1983; Blum & Erel, 1997; Dijkstra *et al*., 2003; Sjögren *et al.,* 2009, p.90; Evans, *pers.com*.) and, in rare cases, where the contents of the archaeological human gut have been recovered, they have been identified. For example, Ötzi the Alpine Ice Man, had micas in his intestines that were thought to be ingested through the grinding of cereal (Müller *et al.,* 2003). Therefore, where possible, mica minerals were also collected and analysed for their bioaccessiblity (see within section 7.3).

7.2. Description of the Unified Bioaccessibility Method

This study employs the Unified Bioaccessibility Method (UBM) developed by the Bioaccessibility Research Group of Europe (BARGE) for examining the bioaccessible inorganic components in soils (Hamilton *et al.* 2015). The UBM simulates the human digestive system by using synthetic digestive fluids which equate to saliva, gastric fluid, duodenal fluid and bile. The synthetic digestive fluids used in the UBM are prepared with inorganic solutions containing inorganic salts (such as KCl, NaCl, etc.) and organic solutions containing organic compounds (such as urea, glucose, etc.). This method also imitates the human body temperature, the length of time expected for each stage of the digestive system and also agitates samples in a manner that mimics the movements produced by the digestive system.

7.3. Materials and Methods

Three lithologies were focused on: the Carboniferous Millstone Grit; the Carboniferous Pennant sandstone; the Ordovician Eskdale granite. The abrasive gritstones and sandstones are well established rocks for milling (Peacock, 2013, p.62-65; Watts, 2014, p.29-30) while the granite was included as it is one of the most radiogenic rocks found within Britain to be used as a grinding stone and thus represents a potentially very high $^{87}Sr/^{86}Sr$ bioaccessible value. The sample locations are given in Figure 7.1.

7.3.1. The geographic source and the mineralogy of the selected rock samples

Millstone Grit is the informal term used for a succession of Carboniferous gritstones found mainly in the Peak District and Pennines of northern England. They were a popular choice for querns and millstones, particularly during the Iron Age and Roman period (Peacock, 2013, p.63-65). These gritstones are a type of sandstone often described as being hard, very coarse-grained and rich in the mineral feldspar. Millstone Grit is dominated by the feldspathic minerals of microcline, plagioclase, orthoclase and also the mica mineral muscovite; calcite can be another common component and some samples of Millstone Grit can have up to 8% apatite (Muir, 1963). All of these minerals are Sr-bearing phases.

There are several known areas where Millstone Grit was believed to have been extensively quarried since the Iron Age, but many have since been abandoned and are difficult to access (Butcher, 1970; Tucker, 1985; Pearson 2000; Peacock, 2013, p.65). The Millstone Grit used in this study was sampled from the still active Stoke Hall Quarry near Grindleford, Derbyshire, opened in 1835. There was enough Sr-isotope biosphere data available for the Peak District that further sampling of plant samples to use as comparison against the UBM results was deemed unnecessary for this study (see chapter 2, section 2.3: Evans *et al.,* 2010).

The Pennant sandstone is a Carboniferous rock described as being lithic (>5% component of lithic fragments) and rich in the minerals feldspar and mica. It can be thinly bedded and varies in colour from a green- or blue-grey to red-brown (BGS Lexicon). The main Sr-bearing phases of Pennant sandstone are predominantly the feldspars such as plagioclase and K-feldspar and the micas which are mainly muscovite (Roe 1987; 1988).

The Pennant sandstone was sampled from the Great Berry Quarry, Brierley, Gloucestershire and is part of the Coal Measures (mud-, silt- and sandstones, interstratified with coal beds) found in the Forest of Dean, near the southern borders of Wales. This sandstone has been used as building stone since the Roman period (Welch & Trotter, 1961; Williams, 1971; Price, 2002) and was used for a variety of other stone tools including honestones, whetstones (both types of sharpening stones for knives etc.), querns and millstones (Moore, 1978; Fowler, 1981; Roe, 1987, 1988; Williams, 1988; Wills & Hoyle, 2007; Allen, 2014). Due to similarities with the near-by Siluro-Devonian Old Red Sandstone (ORS), many Carboniferous sandstones have, in the past, been generalised as part of the ORS Supergroup (Barclay *et al,.* 2005, p.3-5). It is possible that some of the querns or millstones categorized as ORS are in fact made from Pennant sandstone (based on observations in Shaffrey, 2006, p.5-10).

At the time of conducting this study only a few biosphere Sr-isotope values were available for the Forest of Dean (Chenery *et al.*, 2010). Therefore mixed plant samples were collected across the area to define the $^{87}Sr/^{86}Sr$ available in the biosphere. Further details of the Forest of Dean and the geochemical survey conducted can be seen below in section 7.4.

Granites are felsic, intrusive, igneous rocks and will often contain combinations of biotite and muscovite micas, K-feldspar and plagioclase as the main Sr-bearing phases (Hatch, Wells & Wells, 1974). The Eskdale granite was sampled from Beckfoot Quarry in the Lake District, Cumbria. The Beckfoot Quarry is situated in the Eskdale pluton where three types of granite can be found: the medium-grained aphyric (lack of phenocrysts) muscovite granite, known as the ‘normal' granite; a series of microgranites; and a coarse- to very coarse-grained granite (Young, 1999). A sample of the 'normal' granite was taken as it is rich in muscovite.

Granites, although not as popular and extensively used as the abrasive sandstones and gritstones, have been used as querns or millstones in Britain when locally available (Watts, 2014, p.77, 104, 132-133). They are very difficult to shape and grind due to their large crystal sizes (Coope, 1979, p.100), but Bronze Age and Roman querns of Eskdale granite have been recorded at Drigg, Cumbria (Cherry & Cherry, 1968; Cherry, 1988) and several post-medieval millstones have been found in Cumbrian mills (Davies-Shiel, 1978). Plant $^{87}Sr/^{86}Sr$ data is available for the Lake District in chapter 4, section 4.7 of this thesis.

7.3.2. Sample preparation

All the rocks were crushed and ground using standard rock preparation techniques in the Mineral Separation Laboratory at the British Geological Survey (BGS, Keyworth). The <250 µm fraction of each rock was selected for the UBM to mimic the rock that could potentially be ground and make its way into food products. A whole-rock powder was also prepared for each rock.

Large detrital muscovite micas were physically separated out from the >500 µm fraction of the Millstone Grit. Because of their large size, these micas have the potential to be easily plucked from a quern or millstone. Micas were only present in the Millstone Grit and the amount collected was too small to run through the UBM. Instead, they were subjected to a simplified method that mimicked the gastric fluid stage of the UBM and thus the effect of stomach acid only on the minerals.

7.3.3. Unified Bioaccessibility Method (UBM)

Bioaccessibility extractions were undertaken according to the method outlined in Hamilton *et al.* (2015) within the Inorganic Geochemistry Laboratories at the BGS (Keyworth). Briefly, 0.6 ±0.01g of the ground rock sample (<250 µm fraction) was accurately weighed into 85mL Nalgene® oak ridge tubes (ThermoScientific, UK). Simulated saliva and gastric fluid were added to each tube, the pH was adjusted to 1.2 ±0.05, followed by 1 hour of end-over-end agitation in a temperature controlled water bath held at 37°C. The samples were then taken through the stomach and intestine extraction using simulated duodenal and bile fluids (pH adjusted to 6.3 ±0.5 where necessary to account for natural buffering of the sample material). The stomach and intestine extraction involved four hours of end-over-end agitation at 37°C. The samples were then extracted through centrifugation at 6500 RPM for 15 minutes. At the end of each extraction, 10mL of the supernatant was collected and preserved with 0.2mL concentrated (15.9M) HNO_3 prior to analysis and diluted 100-fold with 1% v/v HNO_3. 0.5% v/v HCl before analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The determination of Sr concentration was carried out using an Agilent 7500cx ICP-MS fitted with a CETAC ASX-520 autosampler. Sample introduction from the autosampler to the ICP-MS was controlled by a CETAC ASXpress+ vacuum pump. A quality control (QC) check standard (ULTRA Scientific, USA), containing Sr at 25µg l^{-1}, was analysed at the start and end of each run and after no more than every 20 samples. To overcome polyatomic interferences the ICP-MS collision cell was operated in He mode at a flow rate of 5.5mL min^{-1}. Sample values were calibrated using the standard SpexCertiPREP at 1, 10 and 100µg L^{-1}. The procedural blank for the UBM procedure was 33ng which represents <1% of total Sr yield.

7.3.4. Simplified Leach Method and Standard Whole Rock Dissolution Method

Approximately 0.08g of detrital muscovite mica from the Millstone Grit were exposed to 10mL of stomach acid strength HCl (2.5M) in a Savillex© beaker in a temperature-controlled water bath at 37°C for one hour. The sample was shaken approximately every five minutes to mimic the agitation process of the UBM method. After one hour the supernatant, termed leach, was collected by centrifuging at 3000 RPM for seven minutes and decanting into a newly labelled Savillex© beaker. The leach was then dried down. The HCl-insoluble residues were dissolved using a standard HF-HNO_3 method, and converted to chloride form in preparation for Sr separation.

Approximately 100mg of each of the whole rock powders were dissolved using a standard HF-HNO_3 in labelled Savillex© beakers and converted to chloride form. All samples were centrifuged prior to Sr separation.

Sr was separated from all the samples using Dowex AG 50W-X8 resin columns (Dickin, 1995, p.452). The Sr was then loaded onto single Re Filaments with TaF following the method of Birck (1986), and the isotope composition and concentrations were determined by Thermal Ionisation Mass Spectroscopy (TIMS) using a Thermo Triton multi-collector mass spectrometer. The international standard for $^{87}Sr/^{86}Sr$, NBS987, gave a value of 0.710251 ±0.000005 (n=19, 2SD) during the analysis of these samples. Procedural blanks were in the region of 100pg.

7.4. Geological summary and Geochemical Survey of the Forest of Dean

The Forest of Dean is located in the western part of the county of Gloucestershire (Figure 1.3 in chapter 1), near to the southern borders of Wales and approximately north of the River Severn estuary. The area is known for its coal and iron-ore fields, with evidence of being worked by the Romans (Trotter, 1942), as well as its sandstones (described above in section 7.3.1). The bedrock geology of the Forest of Dean mainly consists of the Siluro-Devonian Old Red Sandstone (ORS), the Carboniferous Limestone Series and the Carboniferous Coal Measures (the coal and iron-ore fields). The bedrock geology of the Forest of Dean study area can be seen in Figure 7.2, alongside plant $^{87}Sr/^{86}Sr$ data.

The Siluro-Devonian ORS can be split into Lower, Middle and Upper sections (Barclay *et al.,* 2005). The majority of the ORS that surround the Forest of Dean are part of the Lower ORS, in which Brownstones dominate. The Brownstones are massive dark red sandstones, described as micaceous, but can also be calcareous, with occasional thin conglomeratic limestones. The Upper ORS contain Quartz Conglomerate and the Tintern Sandstone Group (red, grey and yellow sandstones with bands of quartz conglomerate).

The ORS are then followed by the Carboniferous Limestone Series, which mainly contains varying limestones, dolomites and calcareous mudstones with the addition of the Drybrook Sandstone Group (mainly red coarse-grained sandstones with some conglomerates). It is within the Drybrook Sandstone where most of the iron-ore is found (Trotter, 1942; BGS, 1981, Sheet 233). An unconformity then separates the above with the Carboniferous South Wales Coal Measures, which cover the central area of the Forest of Dean. The Coal Measures mainly comprise of the Pennant Sandstone Formation, a series of coal-bearing mud-, silt- and sandstones, in which the Pennant Sandstone was taken (at Great Berry Quarry, Brierley).

There is limited Quaternary superficial deposits in the Forest of Dean, mainly alluvium and some river terrace and head deposits. These superficial deposits are a mixture of the local rocks and so can vary from being stoneless clays, to containing high amount of debris derived from the Siluro-Devonian Quartz Conglomerate (Trotter, 1942; BGS, 1981, Sheet 233).

Currently a few plant samples surrounding the Forest of Dean from Chenery *et al.* (2010) and Neil *et al.* (2017) have been analysed. The Siluro-Devonian ORS have plant $^{87}Sr/^{86}Sr$ at 0.71133, 0.71293 (Chenery *et al.,* 2010), 0.71064, 0.71076 and 0.71265 (Neil *et al.,* 2017), while the Carboniferous Coal Measures have plant $^{87}Sr/^{86}Sr$ at 0.71185 and 0.71285 (Chenery *et al.,* 2010). The Siluro-Devonian ORS $^{87}Sr/^{86}Sr$ values compare well with the plant $^{87}Sr/^{86}Sr$ on Silurian bedrock in Wales at 0.7117 ±0.0014 (n=10, 1SD: Evans *et al.,* 2010). The Carboniferous Coal Measures compare with water $^{87}Sr/^{86}Sr$ on the Carboniferous Grits of the Midlands and South Devon, at 0.7116 ±0.0003 (n=7, 1SD) and 0.7126 ±0.0001 (n=4, 1SD) respectively (Evans *et al.*, 2010).

In September 2015, a total of 12 locations were visited across the Forest of Dean. The weather over the collection period was cloudy but dry. The plant samples were collected and mixed for each location by the methods described in chapter 3, section 3.2. The field-notes for the mixed plant samples from across the Forest of Dean can be viewed in the Appendix 2. These mixed plant samples then followed the same methods for chemical preparation and Sr-isotope analysis outlined in section 3.3 in chapter 3.

7.5. Results

7.5.1. UBM $^{87}Sr/^{86}Sr$ Results

The whole rock Sr-isotope compositions of the three rocks used are given in Table 7.1. The Millstone Grit has a Sr concentration of 106 ppm and a whole rock $^{87}Sr/^{86}Sr$ of 0.72079 which is within the range, and typical of, previously determined values for this lithology, i.e. 0.71300 - 0.74080 (Diskin, 2002, p.95-96). The Pennant sandstone has a lower Sr concentration of 57 ppm and a higher whole rock $^{87}Sr/^{86}Sr$ of 0.73028. The

Eskdale granite is the most radiogenic sample with a $^{87}Sr/^{86}Sr$ of 0.91373 and has the lowest Sr concentration of 27 ppm, comparable with data from Rundle (1979) who reported a $^{87}Sr/^{86}Sr$ range of 0.76407-1.11430 for this granite.

The bioaccessible Sr from the Millstone Grit had a $^{87}Sr/^{86}Sr$ of 0.71147 and a Sr concentration of 3 ppm; Pennant sandstone yielded a higher bioaccessible $^{87}Sr/^{86}Sr$ of 0.71281 and a similar Sr concentration of 4 ppm; and the Eskdale granite was the most radiogenic at 0.72224 with a Sr concentration of 3 ppm (Table 7.1). In all three cases: there is a significant difference between the whole rock $^{87}Sr/^{86}Sr$ and the bioaccessible component that is accessed during the digestive process, which is displayed in Figure 7.3. The bioaccessible Sr has a lower $^{87}Sr/^{86}Sr$ value than the whole rock and the 3-4 ppm bioaccessible Sr recovered is comparable between all three rock types despite different initial concentrations.

The results from the detrital muscovite micas of the Millstone Grit are in Table 7.2. With $^{87}Sr/^{86}Sr$ = 0.71450 the mica bioaccessible Sr was much less radiogenic than both the whole rock Millstone Grit ($^{87}Sr/^{86}Sr$ = 0.72079) and the indigestible residue ($^{87}Sr/^{86}Sr$ = 0.74858). The relatively high Sr concentration of 270 ppm in the bioaccessible component of these micas, as opposed to 106 ppm from the whole rock of Millstone Grit, suggests that the micas contain inclusions of Sr-rich minerals, such as apatite, that control the bioaccessible component. The bioaccessible $^{87}Sr/^{86}Sr$ value from the micas of 0.7145 thus represents the maximum bioaccessible $^{87}Sr/^{86}Sr$ that the Millstone Grit can contribute as it does not include the UBM second phase of digestive tract exposure nor the effect of other less-radiogenic minerals in the whole rock which reduce the bioaccessible $^{87}Sr/^{86}Sr$ to 0.7115. The indigestible residue from these micas gave the most radiogenic $^{87}Sr/^{86}Sr$ value to be obtained from the Millstone Grit, suggesting that the silicate structure of the detrital micas is robust and unaffected by the digestive processes and so does *not* provide a highly radiogenic source of dietary Sr.

7.5.2. The Forest of Dean: Plant $^{87}Sr/^{86}Sr$ Results

The plant $^{87}Sr/^{86}Sr$ from across the Forest of Dean study area are displayed in Figure 7.2 and 7.4. Altogether, the plant $^{87}Sr/^{86}Sr$ = 0.71132 ±0.00200 (n=11, 2SD), excluding the sample FODL3 which had an elevated $^{87}Sr/^{86}Sr$ at 0.71580. This sample came from Great Berry Quarry, Brierley, the same location as the Pennant sandstone rock sample and so ison the Carboniferous Coal Measures. The plants collected to create this mixed plant sample were rooted into the exposed rock of the quarry (Appendix 2). It is likely a similar situation has occurred as described in Lake District at Beckfoot Quarry (chapter 4, section 4.10.3); where these plants have had access to any bioavailable Sr from the mineral decomposition of the rock they are rooted in, resulting in a more radiogenic value. The $^{87}Sr/^{86}Sr$ value of FOD L3 is elevated above all other mixed plant samples collected across the Forest of Dean by approximately +0.0025, but because of the unusual circumstances in which it has been produced the $^{87}Sr/^{86}Sr$ of FOD L3 should not be seen as a typical biosphere value on this bedrock.

The plant $^{87}Sr/^{86}Sr$ can be split based on the Siluro-Devonian Old Red Sandstones (ORS), the Carboniferous Coal Measures and the Carboniferous Limestone Series (see section 7.4 for further details). The Siluro-Devonian ORS have plant $^{87}Sr/^{86}Sr$= 0.7116 ±0.0021 (n=6, 2SD), while the Coal Measures have plant $^{87}Sr/^{86}Sr$ at 0.71166 (FOD L4) and 0.71237 (FOD L9). The plant $^{87}Sr/^{86}Sr$ from the Coal Measures currently fall with the 2SD of the ORS and so are indistinguishable from one other. However, as expected for marine carbonates formed primarily from shell, the Carboniferous Limestone Series in the Forest of Dean produce a lower and much less variable plant $^{87}Sr/^{86}Sr$= 0.7103 ±0.0002 (n=3, 2SD), although this is still higher than the 0.7092 ±0.0004 (n=11, 2SD) documented by Evans *et al*. (2010). This suggests the limestone biosphere of the Forest of Dean is raised as a result of its proximity to the ORS and Coal Measures or by the inclusion of silicate materials within the limestone series itself (described in section 7.4).

7.6. Discussion

7.6.1. Comparison of bioaccessible $^{87}Sr/^{86}Sr$ from grinding stones with biosphere values contributing to diet.

The Millstone Grit crops out in the Pennines where it is interspersed with Carboniferous limestone giving bimodality to biosphere data in this area depending upon which lithology is the substrate of the food procured by humans. The Carboniferous limestone is well constrained and it gives a plant biosphere $^{87}Sr/^{86}Sr$ value of 0.7092 ±0.0004 (n=11, 2SD: Evans *et al.*, 2010). The Millstone Grit biosphere value of 0.7116 ±0.0006 (n=7, 2SD) was based on mineral water samples (Evans *et al.,* 2010) and may be slightly raised due to the dissolution of minerals by percolating water in direct contact with a rock renowned for producing soft, acidic drinking waters. At Viking Masham in North Yorkshire, one of the few cemetery sites located on Millstone Grit with published human Sr-isotope data, local human values (enamel and dentine) ranged from 0.7096 to 0.7112 (Buckberry *et al.* 2014), i.e. between the plants and the waters.

The bioaccessible $^{87}Sr/^{86}Sr$ from Millstone Grit gave a value of 0.71147 which is within the 2SD range of values obtained for waters above and expected for plants sourced from Millstone Grit regions. In other words, the ingestion of Millstone Grit by people using grinding stones made of this rock or through ingestion of soil in a region of Millstone Grit would not create any anomalous values in their skeletal tissues. If detrital mica were preferentially plucked out of a quern or millstone made of Millstone Grit during grinding and ingested (as was proposed for the micas in the Alpine Ice Man; Müller *et al.*, 2003) the maximum bioaccessible $^{87}Sr/^{86}Sr$ value that could be achieved is 0.71450, in the absence of any other mineral contribution.

The Forest of Dean was a well-known source for querns (Peacock, 2013, p.62-65). Combining the plant biosphere data reported in section 7.5.2 above with other published sources for the Forest of Dean results in the Siluro-Devonian ORS having plant $^{87}Sr/^{86}Sr$= 0.7118 ±0.0019 (n=9, 2SD: Chenery *et al.*, 2010; Neil *et al.,* 2017; section 7.5.2), while the Carboniferous Coal Measures have plant $^{87}Sr/^{86}Sr$= 0.7122 ±0.0011 (n=4, 2SD: Chenery *et al.*, 2010; section 7.5.2). The Carboniferous Limestones Series has the same plant $^{87}Sr/^{86}Sr$= 0.7103 ±0.0002 (n=3, 2SD) reported in section 7.5.2 above.

The Pennant sandstone is part of the Carboniferous Coal Measures. The bioaccessible $^{87}Sr/^{86}Sr$ from Pennant sandstone has a value of 0.71281 which is comparable with the values obtained from plants growing on the Carboniferous Coal Measures and the Siluro-Devonian ORS and medieval humans from sites such as Hereford Cathedral, the majority of whose $^{87}Sr/^{86}Sr$ values range from 0.712 to 0.713 (Evans *et al.*, 2012). Therefore, as with the Millstone Grit, the use of locally sourced grinding stones by local populations would not cause any anomalously high $^{87}Sr/^{86}Sr$ values in skeletal tissues such as tooth enamel.

The transportation of Millstone Grit or Pennant sandstone grinding stones into a region of different geology may be problematic to provenance studies if the target biosphere is characterised by significantly lower or higher $^{87}Sr/^{86}Sr$. In this scenario there is the potential for the ingested rock to contribute non-local dietary $^{87}Sr/^{86}Sr$, causing human $^{87}Sr/^{86}Sr$ values to diverge from the predicted local range. In some localities, both the Millstone Grit and Pennant sandstone can occur in proximity to Carboniferous limestones and in this scenario the bioaccessible $^{87}Sr/^{86}Sr$ from grinding stones will be approximately 0.002 higher than the $^{87}Sr/^{86}Sr$ of plants sourced from limestone lithologies, i.e. 0.7092 ±0.0004 (n=11, 2SD; Evans *et al*., 2010). Abrasive sandstones, particularly the prized Millstone Grit, have been extensively traded and transported as grinding stones in Britain (Peacock, 2013, p.62-65) and so have the potential to be used and their rock grit unintentionally consumed in a variety of different geological regions. In the case of Millstone Grit or Pennant sandstone, however, neither would raise human skeletal $^{87}Sr/^{86}Sr$ above 0.71281 and cannot thus explain human $^{87}Sr/^{86}Sr$ of 0.713 and above.

The Eskdale granite crops out in the Eskdale area of the Lake District, Cumbria, which has an old and complicated geological structure (chapter 4, section 4.7). The Ordovician sedimentary rocks of the Skiddaw Group have plant $^{87}Sr/^{86}Sr$= 0.7102 ±0.0007 (n=4, 2SD), with an elevated value at 0.71227 (LD L14), while the Borrowdale Volcanic Group have $^{87}Sr/^{86}Sr$= 0.7098 ±0.0007 (n=5, 2SD), with one elevated value at 0.71221 (LD L12). Plant $^{87}Sr/^{86}Sr$ at 0.71053 (LD L9), 0.71298 (LD L17) and 0.71471 (LD L8) are record on the Eskdale granites. The bioaccessible $^{87}Sr/^{86}Sr$ of Eskdale granite is 0.72224 which considerably exceeds the $^{87}Sr/^{86}Sr$ range of plants naturally extracting bioaccessible Sr from this lithology. Unlike the Pennant sandstone and Millstone Grit, this granite has the potential to raise human $^{87}Sr/^{86}Sr$ values beyond any current $^{87}Sr/^{86}Sr$ biosphere values found naturally within Britain (see Evans *et al.*, 2010). However, the outcrop area of the Eskdale granite is insignificant compared to that of the sandstones and gritstones of the Carboniferous and in general granites were not commonly used as grinding stones in Britain; why seek out a stone that is rare, less accessible and does not do the job as well as the abrasive sandstones, such as Millstone Grit, which were readily available in most regions?

7.6.2. Food vs. rock grit: modelling the amount of ingested rock grit required to change human $^{87}Sr/^{86}Sr$

Although the UBM results demonstrate that there is potential for human $^{87}Sr/^{86}Sr$ to be changed by ingested grit, particularly if using imported 'exotic' stones, it will never be the case that grit is the only thing ingested. When, therefore, can ground rock (or minerals), produced through the use of grinding stones, realistically affect the Sr-isotope contribution to the human diet? The controlling factors are the difference in isotope composition between the bioaccessible component of the rock (or mineral) and the main Sr-isotope composition of the diet, the relative concentration of Sr in both components, and the amount of rock that can sensibly be incorporated within the diet. In order to model such an eventuality, an assessment of the amount of ground rock that would be produced and incorporated into food such as bread is required.

Estimates of quern and millstone wear and erosion rates will depend on the hardness of the rock being used (Biot, 2011; Buonasera, 2015), but an estimated contribution of 1-2% grit from the grinding stones in milled flour seems to be realistic. Biot (2011) for example, states that around 2% of greensand (a type of sandstone) was present in grain ground by these querns. Given that 4kg of flour is the maximum that can be produced from one quern in one hour (Peacock, 2013, p.126-128), around 80g (2%) could be rock grit. Once the flour is produced the potential percentage grit component in the diet is further diluted by the other dietary components, including those used in bread making. The calculations that follow are based on bread in the Medieval period of Britain and are a *theoretical model* of how the unintentional ingestion of grit from grinding stones in flour, through the consumption of bread could contribute to human $^{87}Sr/^{86}Sr$ values.

There are a variety of bread recipes known from Medieval Britain, often ranked by the quality of flour used to make the loaves. White flour made from wheat was predominately used in the best loaves, such as the manchet loaf, and wholemeal flour in the lesser loaves, whilst the poorest loaves would have a mixture of other grains such as rye or barley (Brears, 2015, p.125-131). The ingredients below produced one large wholemeal bread loaf, converted to decimal measurements (Brears, 2015, p.130-131):

- 900g (strong) wholemeal flour
- 550mL water at 24^{o}C
- 15g dried yeast (instead of the sourdough culture they would have used)
- 1 g salt

(900+440+15+15 = 1370, 18/1370 = 0.013*100 = 1.3% could be rock grit if 20% of water evaporates during baking)

In this loaf, a maximum of 2%, i.e. 18g, of the wholemeal flour can be considered rock grit. During the baking process approximately 10-20% of the water content can be lost through evaporation (Hamelman, 2004), which is approximately 55-110mL of the water in the loaf recipe above. Assuming that none of the other ingredients are contaminated with grit and 20% of the water is lost through evaporation in the baking process, the grit makes up approximately 1.3% of this bread loaf (by weight). Bread has been a major contribution to the diet in Britain since the Neolithic (Peacock, 2013, p.17-21), but it is in the Medieval period when consumption was known to be particularly high. An upper limit for the proportion of bread in the Medieval diet was c. 74% (by weight and calorific intake: Dyer,1988, p.25-27) and if 1.3% of the bread was grit, c. 0.96% of the total diet would be rock grit from the milling process.

Consequently, if this rock grit is to impact on dietary Sr and affect human $^{87}Sr/^{86}Sr$ values it needs to be able to significantly change the Sr-isotope composition of the diet when present at c. 0.96%. The contribution to diet can be calculated using a two component, or end-member, mixing diagram (Faure, 1998). For an individual who used querns or millstones composed of Millstone Grit (component 1) to grind grain, the bioaccessible component of the ground rock ingested would contribute $^{87}Sr/^{86}Sr$ of 0.71147 at 3 ppm Sr concentration in the digestive tract. If in this scenario the individual was procuring and consuming plants grown in a region of Chalk (component 2), the plants consumed as the bulk of the diet can be estimated to have an average $^{87}Sr/^{86}Sr$ of 0.70808 and 9 ppm Sr concentration (based on Warham, 2011, p.88).

Table 7.3 shows the results of mixing component 1, the ground Millstone Grit, with component 2, plants grown in soil overlying Chalk bedrock from 0 to 100% contribution. At 0.96% grit the $^{87}Sr/^{86}Sr$ contribution to human diet has only been increased by +0.00001. At the 5th significant figure, this change in the $^{87}Sr/^{86}Sr$ value can be considered of little importance: it is largely within 2SD measurement error. Moreover, when interpreting and discussing Sr-isotope compositions in mobility and provenance studies any change to the 4th significant figure of the ratio can be considered irrelevant: siblings can vary by 0.0002 (Montgomery, 2002, p.146) and cattle raised in the same herd by 0.0006 (Towers, 2013, p.123-124). Even if the Millstone Grit is replaced by the considerably more radiogenic Eskdale granite ($^{87}Sr/^{86}Sr$ of 0.72224 and 3 ppm) the change is still at the 5th significant figure at a 0.96% contribution, increasing the $^{87}Sr/^{86}Sr$ value only by +0.00005.

Up to 8% of the diet needs to be from ground Millstone Grit before the $^{87}Sr/^{86}Sr$ is affected by +0.0001. To achieve a significant change of +0.001 requires a 56% contribution, which is extremely unrealistic (Table 7.3). For the Eskdale granite, a 2% contribution of ground rock in the diet is needed to change the $^{87}Sr/^{86}Sr$ by +0.0001 and a 19% contribution to change it more significantly by +0.001. These are of course only approximated percentages and a 2-8% unintentional grit component in the diet may not seem unrealistic. However, the calculations are based on a maximum possible grit production in the milling process and a Medieval diet, when records document a high consumption of bread (up to 74%; Dyer, 1988, p.25-27). It would seem to be difficult to unintentionally introduce more than 1% contribution of rock into the human diet. Therefore, although ground rock (or minerals), via the use of querns and millstones, can provide a source of non-local bioaccessible $^{87}Sr/^{86}Sr$ they would be very rarely consumed in enough quantity to have an impact on human $^{87}Sr/^{86}Sr$ values and result in the false identification of an individual as non-local.

There may of course be exceptions to this if an individual was intentionally ingesting soil and grit, e.g. pica and geophagy, or if food was being deliberately contaminated. For example it was not uncommon for 19th-century bakers to add chalk or other substances to their bread flour (Accum, 1820). Research into pica and geophagy has revealed that the practice of consuming non-food substances has been remarkably prevalent across many human cultures over many time periods, particularly, and crucially given when deciduous and permanent teeth are forming, in pregnant women and children (Young, 2012; Henry *et al*., 2013 p.189-191). The consumption of earth or soil-like substances via geophagy typically consisted of clays and chalks (Young, 2012, p.95; Henry *et al*., 2013 p.189-191).

If certain individuals did intentionally consume clays or chalks in Britain, $^{87}Sr/^{86}Sr$ values ranging from 0.7097 ±0.0014 (n=14, 2SD) to 0.7117 ±0.0028 (n=10, 2SD) for the clays (depending on bedrock lithology) and 0.7082 ±0.0008 (n=9, 2SD) for the chalks (Evans *et al.,* 2010) could potentially be bioaccessible. The bioaccessible $^{87}Sr/^{86}Sr$ from clays and particularly the homogenous carbonate rocks in Britain, which include the chalks, are likely to follow the same pattern shown by the Millstone Grit and Pennant sandstone in this study, being on par with $^{87}Sr/^{86}Sr$ provided by the biosphere on such lithologies. So, if clays or chalks were consumed locally it is unlikely that they would create any anomalous $^{87}Sr/^{86}Sr$ values in the human skeletal tissues. If clays or chalks were consumed in different geological regions with a significantly lower or higher biosphere $^{87}Sr/^{86}Sr$, then the human $^{87}Sr/^{86}Sr$ could diverge from the expected biosphere $^{87}Sr/^{86}Sr$ values, particularly as carbonate-dominated clays and chalks are likely to have higher bioaccessible Sr concentrations than displayed by the silicate rocks in this study. If the mixing model used above was switched, so the rock grit of chalk was consumed on a Millstone Grit Sr-isotope biosphere instead, theoretically, 13% of the diet would still need to be from the deliberate consumption of grit to lower the $^{87}Sr/^{86}Sr$ significantly, i.e. by -0.001.

However, the practice of geophagy can be extremely difficult to recognise in the archaeological record (Henry *et al*., 2013, p.190) and in Britain it is not well known. Therefore, if an archaeological individual excavated in Britain has a non-local $^{87}Sr/^{86}Sr$ value it appears more realistic to infer that they are non-local rather than participating in geophagy or pica, unless evidence strongly suggests otherwise.

7.7. Conclusions

The UBM method has shown that Sr in rock grit, whether accidently ingested via the use of grinding stones or deliberately through pica or geophagy, is rendered bioaccessible by the strong acids of the human gut. However, a significant alteration of human skeletal $^{87}Sr/^{86}Sr$ as a result of ingested rock grit Sr, evading the transmission via plants, is likely to occur only in unusual behaviours such as pica, geophagy, or the deliberate contamination of food. In such circumstances, clays or chalks are commonly utilised and it is theoretically estimated that such lithologies would still need to comprise >13% of the diet (by mass and calorific intake) on a regular basis to significantly shift human skeletal $^{87}Sr/^{86}Sr$.

Rock grit unintentionally consumed as a result of using quern or millstones to grind grain is unlikely to equate to more than 1% of the diet and the $^{87}Sr/^{86}Sr$ of bioaccessible Sr from Millstone Grit or Pennant sandstone falls within the observed biosphere $^{87}Sr/^{86}Sr$ ranges for these rocks. The Eskdale granite produces bioaccessible $^{87}Sr/^{86}Sr$ which exceeds that available from plants in granitic regions. Nonetheless, at the 1% level, regardless of the grinding stone's lithology or the local Sr-isotope biosphere, ingested grit will not result in a significant change in human $^{87}Sr/^{86}Sr$ values. Consequently, the use of querns or millstones and the regular unintentional consumption of their grit, whether of locally-derived or imported rock, will have a negligible effect on human $^{87}Sr/^{86}Sr$ data and will neither produce anomalously high skeletal $^{87}Sr/^{86}Sr$ values nor false migrants. Even the intentional consumption of rock, clays or soils through geophagy or pica, which is difficult to identify in the archaeological record, is unlikely to adversely affect skeletal $^{87}Sr/^{86}Sr$. Moreover, this deliberate targeting of clays and chalks which tend to be characterised by low $^{87}Sr/^{86}Sr$, i.e. <0.709, and so is also an unlikely source of high $^{87}Sr/^{86}Sr$ >0.714 in archaeological humans.

The results of this study thus provide reassurance to researchers using Sr-isotope analysis to identify migrants in Britain and elsewhere that non-local or unusually high $^{87}Sr/^{86}Sr$ values cannot be explained by the direct ingestion of rock grit, clays or soils.

7.Tables and Figures

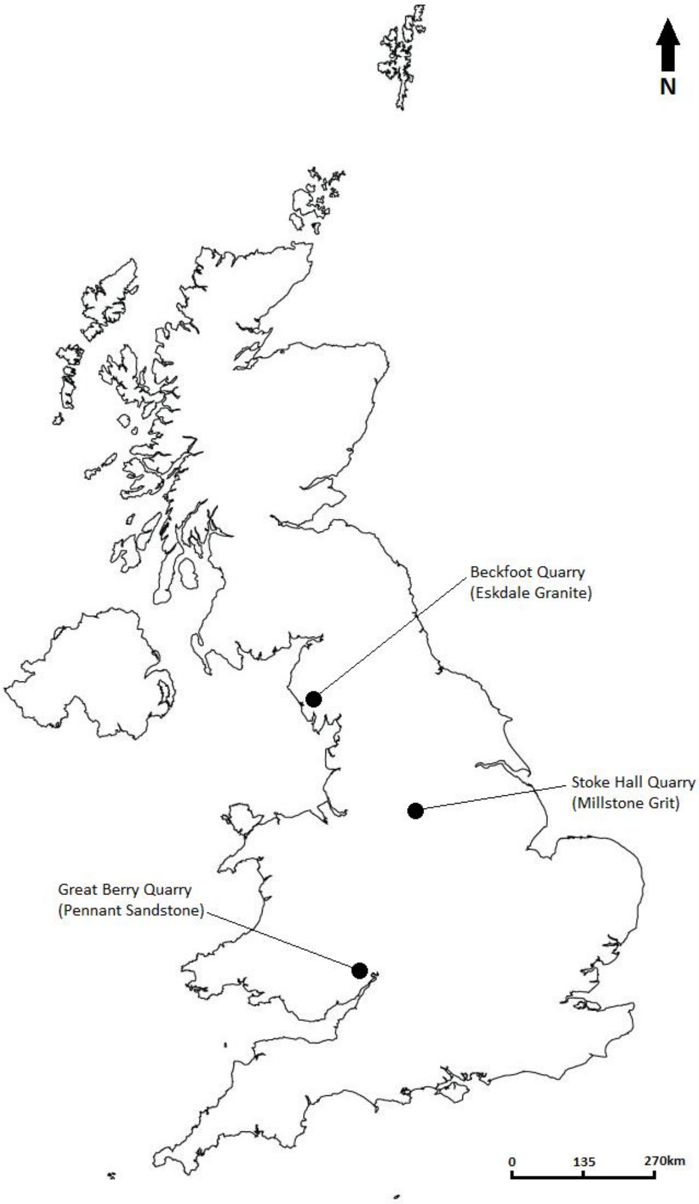


Figure 7.1. The locations of the rock samples: Millstone Grit, Stoke Hall Quarry, Peak District (Derbyshire); Pennant Sandstone, Great Berry Quarry, Forest of Dean (Gloucestershire); Eskdale granite, Beckfoot Quarry, Lake District (Cumbria).

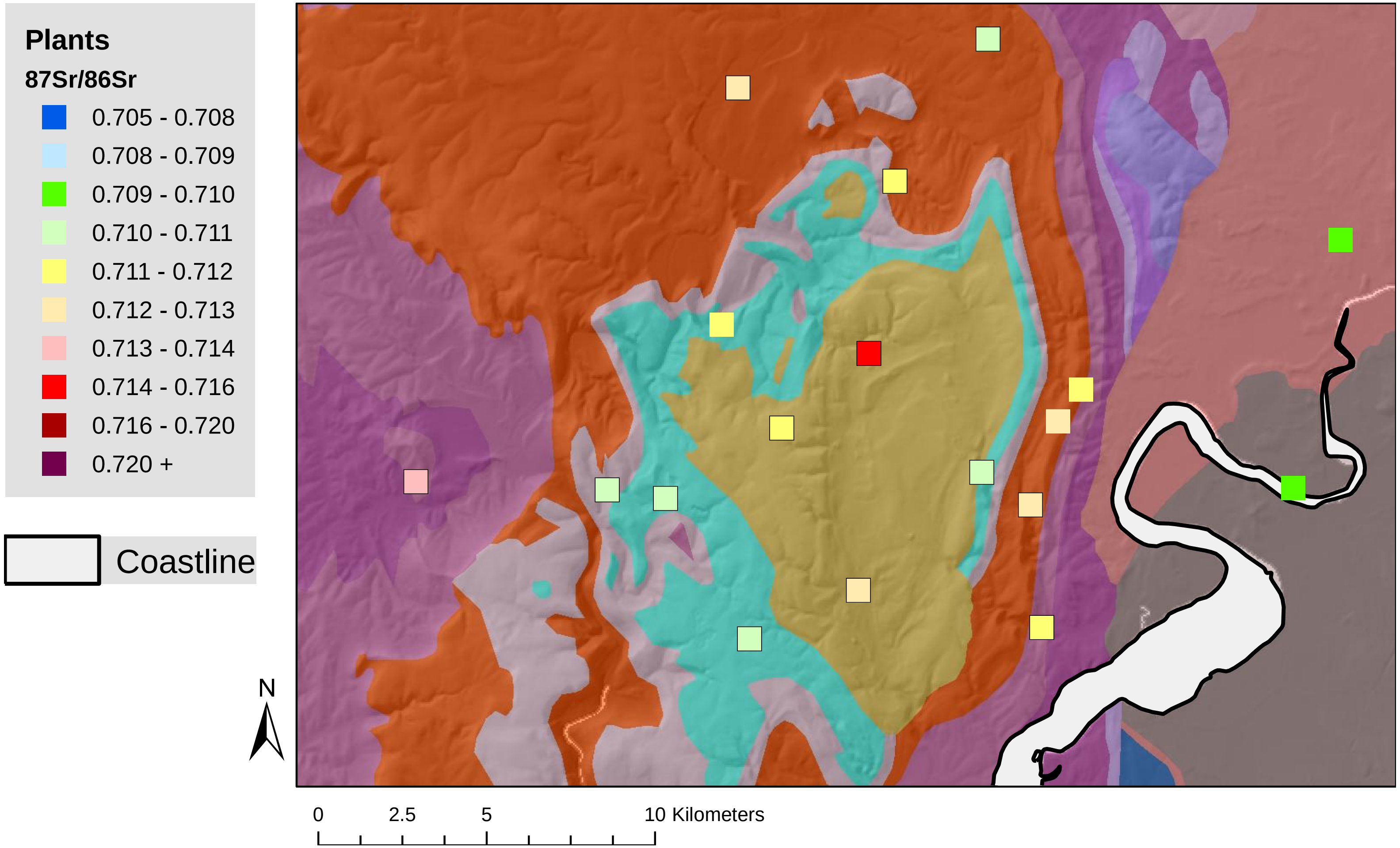


Figure 7.2. The plant $^{87}Sr/^{86}Sr$ from across the Forest of Dean study area, alongside GIS data of the 1:625000 Bedrock Geology map (BGS, DiGMapGB, 2007). The main legend for the Bedrock geology can be seen in Figure X. The other plant $^{87}Sr/^{86}Sr$ (squares not outlined) is from Chenery *et al.* (2010).

Table 7.1. Sr concentrations and $^{87}Sr/^{86}Sr$ of the whole rock samples and the bioaccessible Sr derived from the rock grit determined from the UBM.

Rock Sample	Whole Rock Sr ppm	Whole Rock $^{87}Sr/^{86}Sr$	Bioaccessible Sr ppm	Bioaccessible $^{87}Sr/^{86}Sr$	ΔWhole Rock-Bioaccessible $^{87}Sr/^{86}Sr$
Millstone Grit	106	0.72079	3	0.71147	0.00932
Pennant Sandstone	57	0.73028	4	0.71281	0.01747
Eskdale Granite	27	0.91373	3	0.72224	0.19149

Table 7.2. Sr concentration and $^{87}Sr/^{86}Sr$ of the detrital muscovite micas from the Millstone Grit.

Millstone Grit: Detrital Mica	Sr ppm	$^{87}Sr/^{86}Sr$
Bioaccessible Component (leach)	270	0.71450
Indigestible Residue	24	0.74858

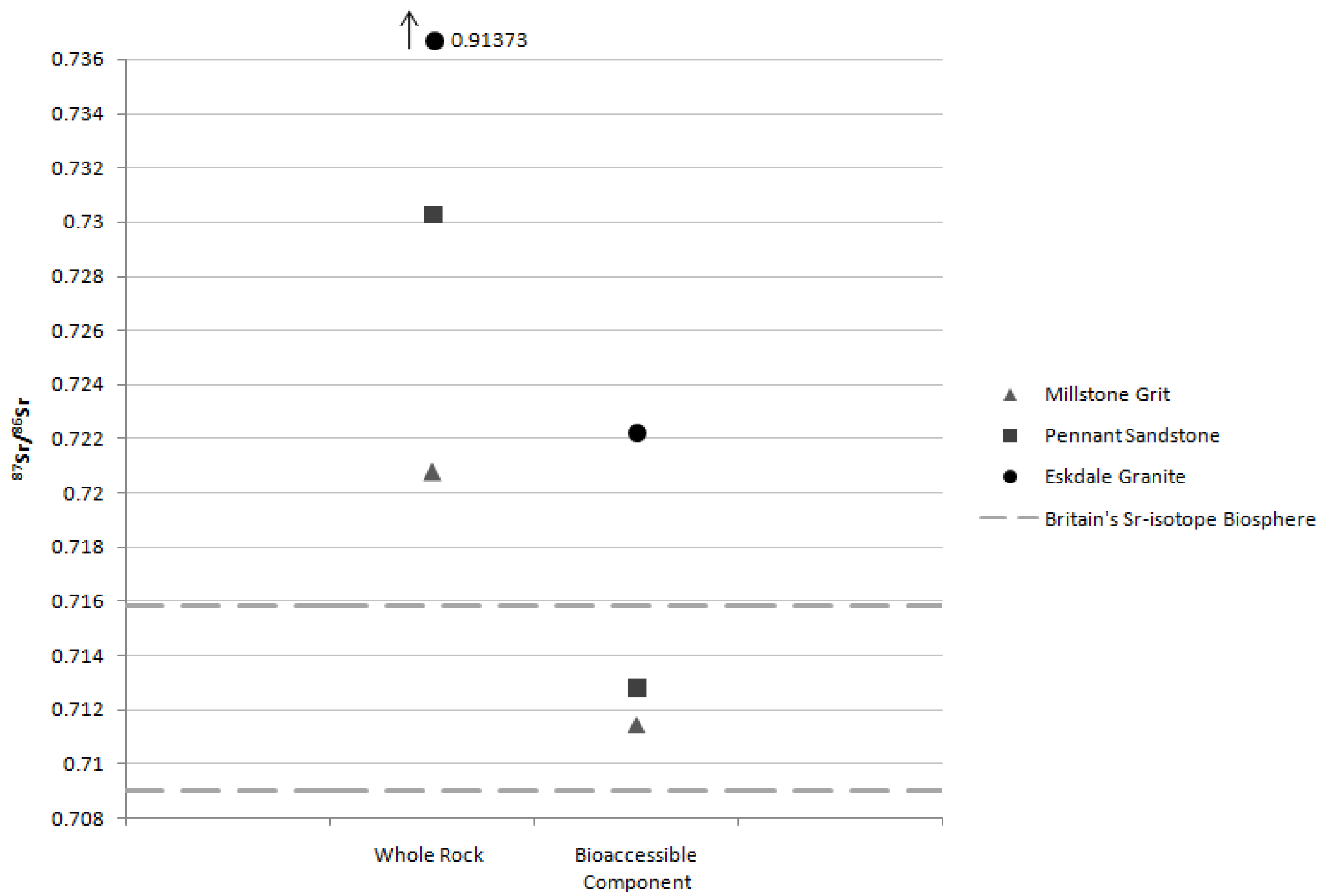


Figure 7.3. The $^{87}Sr/^{86}Sr$ of the whole rock vs. the bioaccessible component of the ground rock determined by the UBM.

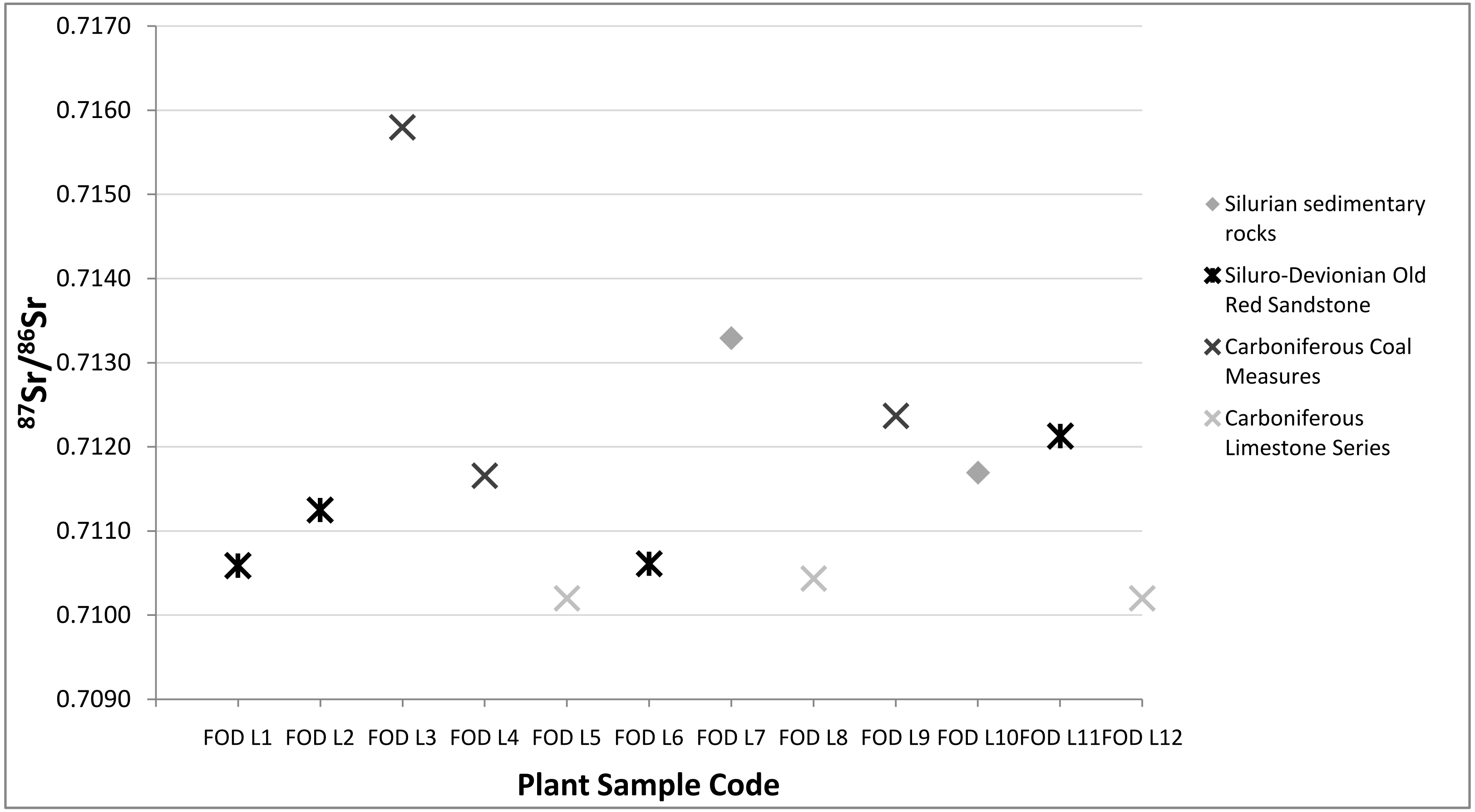


Figure 7.4. The plant $^{87}Sr/^{86}Sr$ collected from across the Forest of Dean study area, based on the age of the main bedrock geology from which they were taken.

Table 7.3. The results of the mixing model from 0 to 100% contribution of component 1 (ground Millstone Grit) to component 2 (plants grown in soil overlying Chalk bedrock). The 0.96% contribution is highlighted in bold and italics and the other two contributions in italics represent when a significant change occurs in the $^{87}Sr/^{86}Sr$ value.

% component 1	$^{87}Sr/^{86}Sr$ mixture
0.00	0.70808
0.50	0.70809
0.96	***0.70809***
1.00	0.70809
5.00	0.70814
8.00	*0.70818*
10.00	0.70820
20.00	0.70834
30.00	0.70850
40.00	0.70870
50.00	0.70893
56.00	*0.70909*
60.00	0.70921
70.00	0.70956
80.00	0.71002
90.00	0.71062
100.00	0.71147

8. Discussion of the high Sr-isotope biospheres in Britain: can a home in Britain be found for people with high $^{87}Sr/^{86}Sr$?

8.1. Radiogenic Sr-isotope biospheres in Britain

8.1.1. The maximum biosphere $^{87}Sr/^{86}Sr$ in Britain

None of the 151 plant samples analysed in this thesis have recorded $^{87}Sr/^{86}Sr$ values >0.720, however 20 samples have recorded values >0.714 (Table 8.1). Of these, 13 are located in the Cairngorms National Park in Scotland, with the highest plant $^{87}Sr/^{86}Sr$= 0.71820 (SCOT GL3). The other seven samples are located in England, with the highest plant $^{87}Sr/^{86}Sr$ = 0.71613 (SHC L5). If combined with previous biosphere $^{87}Sr/^{86}Sr$ values >0.714 described in chapter 2 (section 2.3.1, Table 2.1) and Shand *et al.* (2007), there are 82 biosphere$^{87}Sr/^{86}Sr$ values >0.714 across Britain, with 43 located in Scotland, 36 in England and Wales and four in Northern Ireland (Figure Xi). However, three of the samples from England and Wales (LD L8, FOD L3 in this thesis and JMPD_08 from NIGL, unpublished results) are known to be plants directly rooted in exposed rock and so should not be seen as typical of their local biosphere $^{87}Sr/^{86}Sr$. These are discussed in section 8.1.4 further below.

There are 828 biosphere $^{87}Sr/^{86}Sr$ available across Britain (Figure Xi), but values >0.714 (n=82) only represent the upper 10% of the known British values approximately. Britain has an area of approximately 209, 331km^2 in total. The area biosphere $^{87}Sr/^{86}Sr$ >0.714 currently occupy in Britain is approximately 5830km^2. Therefore only 2.8% of Britain has biosphere $^{87}Sr/^{86}Sr$ >0.714, so despite the occurrence such values, they are still spatially rare in Britain.

8.1.1.1. The maximum biosphere $^{87}Sr/^{86}Sr$ of Scotland

The area north of the Cairngorms mountains, around Aviemore and Glenmore has produced biosphere $^{87}Sr/^{86}Sr$ values >0.714 consistently (chapter 5, section 5.4.1) and it can be defined as generating elevated $^{87}Sr/^{86}Sr$ in the overlying biosphere in the upper 10% of the known British values approximately. These samples are found around the base of the Cairngorm and Monadhliath Plutons, potentially on the thermal aureoles which are discussed in section 8.1.2 below. The highest $^{87}Sr/^{86}Sr$ value from a plant sample is SCOT GL3 at 0.71820, while the highest value from a water sample is EBP-47 at 0.71937 (Evans *et al.,* 2010). No other proxy types have been collected from the area around Aviemore and Glenmore. Altogether, north of the Cairngorms mountains can be defined as a biosphere with radiogenic values in the upper regions of the current British biosphere dataset, having $^{87}Sr/^{86}Sr$ = 0.7174 ±0.0049 (n=7, 2SD: chapter 5, section 5.4.1 and 5.5).

The Silurian Cairngorm suite that forms the Cairngorm mountains, as well as the Ordovican Grantown Pluton, have also produced elevated biosphere values, albeit lower than the area that surrounds their base, described above (chapter 5, section 5.4.1). The highest plant $^{87}Sr/^{86}Sr$ = 0.71672(EBP-46a: Evans *et al*., 2010), while a similar value in this thesis at 0.71639 (SCOT GL8) shows that high $^{87}Sr/^{86}Sr$ >0.716 are reproducible in the biosphere on the Cairngorm suite. The highest water $^{87}Sr/^{86}Sr$ = 0.71571 (Aberd-2: Evans *et al.,* 2010). Altogether the Cairngorm suite have biosphere $^{87}Sr/^{86}Sr$ = 0.7155 ±0.0014 (n=8, 2SD). The Ordovician Grantown Pluton has a plant $^{87}Sr/^{86}Sr$ at 0.71463 (SCOT L25). For those wanting to use the Grantown Pluton in their migratory or mobility studies the analysis of more biosphere samples would be useful to see if this value is reproducible. The rest of the mixed plant samples from the Cairngorms National Park that have values >0.714 are sporadic, being among the lower plant $^{87}Sr/^{86}Sr$ values of the Precambrian Dalradian Supergroup (~0.708 to 0.712: chapter 5, section 5.4.2 and 5.5).

None of the plant samples with $^{87}Sr/^{86}Sr$ values >0.720 from the Grampian terrane in Scotland (see Figure 5.3 in chapter 5) have been reproducible. This includes the plant samples EBP-15 (0.72513) EBP-41 (0.72093) and EBP-48 (0.72660) from Evans *et al.* (2010). The first two plant samples, which are based on the Precambrian Dalradian Supergroup, have been described as hotspots, with no lithological reason for their high $^{87}Sr/^{86}Sr$. So far, the highest plant $^{87}Sr/^{86}Sr$ values on the Dalraidan Supergroup are from the quartzites, at 0.7141 ±0.0013 (n=5, 2SD), which is a significant difference of approximately -0.0069 - 0.0111 compared to hotspot samples. The plant sample EBP-48 is near the base of the Cairngorms Pluton, near Glenmore and assumed to be a result of the Cairngorm granite. Again though, there is a significant difference of approximately -0.0084 between EBP-48 (0.72660) and the next highest plant sample seen in the

Glenmore area, SCOT GL3 (0.71820). It is possible that the plant samples with values >0.720 in Evans *et al.* (2010) may have been contaminated with grit or suffered from mud-splash, which has resulted in their high $^{87}Sr/^{86}Sr$ values. As the plant samples collected in this thesis were created mainly from the collection of foliage freshly picked from tree species, mud-splash and grit contamination from the soil was not a concern during Sr-isotope analysis (chapter 3, section 3.2.2). Even dust contamination on the surface of tree leaves has been shown to be negligible in Sr-isotope analysis (Warham, 2011, p.144-150). It is unlikely that these radiogenic values >0.720 will be reproducible by plants in the Grampian terrane.

The water sample JMW_23, with $^{87}Sr/^{86}Sr$ at 0.72065 (Evans *et al.,* 2010), located around the village of Chapeltown (Ballindalloch) is believed to be influenced by the granitic rocks of the nearby Silurian Glenlivet intrusion (chapter 5, section 5.4.2). The plant samples collected in and surrounding the village of Chapeltown have not recorded values >0.720, the highest being SCOT CTL5 at 0.71426. However, this does not mean this water sample is anomalous. Water samples can often produce more radiogenic values than plants collected in the same area, as it depends on where their source of Sr originates and hence what minerals they leach as they filter through rocks, resulting in $^{87}Sr/^{86}Sr$ values which are not normally released into soils through surface processes (chapter 3, section 3.1; chapter 5, section 5.4.1). The water sample EBP-47 at 0.71937 (Evans *et al.,* 2010), at the base of the Cairngorm Pluton, near Glenmore, is also has a higher $^{87}Sr/^{86}Sr$ value than the plant samples collected from the same area.

Further stream water samples from Glensaugh, which are approximately 5km away from the granitic Mount Battock Pluton, have water $^{87}Sr/^{86}Sr$ range of 0.7177 - 0.7187, with an average water $^{87}Sr/^{86}Sr$ = 0.7184 ±0.0003 (n=16,1SD: Bacon & Bain, 1994). The main source of Sr for these stream waters likely comes from the minerals within the granitic rocks of the Mount Battock Pluton upstream, rather than the Precambrian Dalradian Supergroup they are based on.

Overall the Cairngorms National Park, and the Grampian terrane as a whole, has a maximum plant $^{87}Sr/^{86}Sr$ = 0.718, while for water ~0.720 is expected. It would be beneficial to conduct further analysis of biosphere samples on and around the granitic rocks of late Silurian to early Devonian Argyll suite (chapter 5, section 5.1.3), approximately 60km south-west of the Cairngorm suite, as only three plant samples are available from this area with values of 0.70914 (ARD 01), 0.71228 (ARD 14) and 0.71619

(ARD 15) (Evans *et al.,* 2010). It is expected that the large granitic plutons of the Aryglll suite may produced similar elevated values as found on and around the plutons of the Cairngorms suite.

As for the rest of Scotland, the $^{87}Sr/^{86}Sr$ >0.714 (Table 2.1, chapter 2) are currently in support of the maximum plant and water $^{87}Sr/^{86}Sr$ stated above for Grampian terrane (see Figure 5.3 in chapter 5 for positions of the terranes in Scotland). They include four plant and two water samples, from the 21 biosphere samples, taken across the mainland of the Northern Highland terrane (Evans *et al.,* 2010). The plant $^{87}Sr/^{86}Sr$ = 0.7178 ±0.0022 (n=4, 2SD), while the water samples have values at 0.71667 (EBP-04) and 0.71738 (EBP-25). Then there are a further six plant and three water samples, from the 51 biosphere samples, taken across the Hebridean terrane (Montgomery *et al.,* 2007; Evans *et al.,* 2009; 2010). The plant $^{87}Sr/^{86}Sr$ = 0.7180 ±0.0026 (n=6, 2SD), all of which are located on the Isle of Skye (Evans *et al.,* 2009), while the water $^{87}Sr/^{86}Sr$ = 0.71785 (HARW-3), 0.71821 (HARW-5), 0.72335 (HARW-1) and are located on the Outer Hebrides (Evans *et al*., 2010). The biosphere data from the Northern Highland terrane is sparse (n=21) and would benefit from furthering sampling, which could result in new maximum biosphere $^{87}Sr/^{86}Sr$ data.

At present though, Scotland has a the maximum plant $^{87}Sr/^{86}Sr$ = 0.718, while water values are expected to be ~0.720 maximum.

8.1.1.2. The maximum biosphere $^{87}Sr/^{86}Sr$ of England and Wales

There are 36 biosphere $^{87}Sr/^{86}Sr$ values >0.714 located in England and Wales, 15 are plant samples (Table 8.1 and Table 2.1, in chapter 2), and 21 are water samples (Shand *et al.,* 2007). Three out of the 15 plant samples are known to be plants that were rooted in exposed rock (LD L8, FOD L3 and JMPD_08) and are discussed in section 8.1.4 below.

The deep groundwater from borehole VB 1, with $^{87}Sr/^{86}Sr$= 0.71521 (Shand *et al.,* 2007) is currently the highest water value in England and Wales. The rest of the water values >0.714 range from 0.7140-0.7149 (n=20) and they are all on the Lower Palaeozoic shales and mudstones in the catchment of Plynlimon, central Wales (Shand *et al.,* 2007). However, altogether the ground and stream water samples from the catchment of

Plynlimon record $^{87}Sr/^{86}Sr$ between 0.7093 - 0.7152 (n= 45: Shand *et al.*, 2007). These values seem to reflect the heterogeneous nature of the bedrock lithologies and have mean $^{87}Sr/^{86}Sr$ at 0.7139 ±0.0030 (n=25, 2SD) for the ground waters and 0.7130 ±0.0016 (n=20, 2SD) for the stream waters. Just the ground waters on the Ordovician bedrock have $^{87}Sr/^{86}Sr$ = 0.7130 ±0.0008 (n=11, 1SD: Evans *et al.,* 2010).

Apart from the catchment of Plynlimon in central Wales above, all the other water samples in England and Wales have $^{87}Sr/^{86}Sr$ values <0.714 and only four samples with values >0.713. They include two mineral water samples reported in Montgomery *et al.* (2006), with $^{87}Sr/^{86}Sr$ at 0.71329 (JMW_07) and 0.71393 (JMW_05) based on the Precambrian Malvern Complex of the Malvern Hills (England) and the Silurian mudstone of Radnor Hills (Wales) respectively. Then there are a further two water samples in Cornwall (England), with $^{87}Sr/^{86}Sr$ at 0.71327 (HWP-5) and 0.71363 (HWP-10), based on Carboniferous sedimentary rock and the Carboniferous-Devonian granitic rocks of the Dartmoor Pluton respectively. The water sample HWP-5 is among other water $^{87}Sr/^{86}Sr$ between 0.7100-0.7126 (n=9) on the same Carboniferous sedimentary rocks, while the water sample HWP-10 on the Dartmoor Pluton has a difference of approximately +0.0022 compared to a plant $^{87}Sr/^{86}Sr$ at 0.71144 (CORN-5) also taken on the pluton (Evans *et al.,* 2010).

For the remaining 12 plant values with elevated $^{87}Sr/^{86}Sr$ above predicted values for the area, all but two (FISH-4 and SF L3: Evans *et al.,* 2010; chapter 6) are located near or along the Welsh Border. Five are found in the Malvern Hills (chapter 4, section 4.2: Chenery *et al.,* 2010: Evans, *pers.com*.), three are located near Church Stretton (CS L2, CS L3 and CS L12; chapter 4, section 4.4) on the outskirts of the Precambrian Longmydian bedrock, one is located near the Precambrian Stanner-Hanter Complex (SHC L5; chapter 4, section 4.6), but is based on Silurian Ludlow sedimentary rocks and then one is located near Hell's Mouth, Powys, Wales (USK-04, Table 2.1), also based on Silurian Ludlow sedimentary rocks. The latter five plant samples are all based within the Welsh Borderlands Fault System, which contains the largest Precambrian inliers of England and Wales (see Figure 3.1, chapter 3: Pharaoh & Gibbons, 1994; Pharaoh & Carney, 2000).

The first isolated, elevated value, FISH-4 at 0.71467 (Evans *et al.,* 2010), is located amongst the Cambrian mountains in Wales, near the town of Llanidloes (Powys), and is again on the Silurian sedimentary rocks, but this time dating to the Llandovery. A further three plant samples on this bedrock have $^{87}Sr/^{86}Sr$ = 0.71329 (S-WALES 29), 0.71353 (S-

WALES 27) and 0.71399 (S-WALES 31: Evans, unpublished results; *pers.com*.), but altogether the Silurian Llandovery bedrock have a plant $^{87}Sr/^{86}Sr$ = 0.7119 ±0.0045 (n=8, 2SD: Evans *et al.*, 2010; Evans, unpublished results; *pers.com*.). The other isolated and elevated value, SF L3 at 0.71757, is located within the ancient woodland of the Sherwood Forest Nature Reserve (Nottinghamshire, England) and is based on the Triassic Sherwood Sandstone Group. Its value is believed to be a result of the woodland effect (chapter 6). Another two plant samples believed to be influenced by Sherwood Forest have $^{87}Sr/^{86}Sr$ at 0.71218 (SF L4) and 0.71358 (SF L1), while plant samples taken around agricultural land have plant $^{87}Sr/^{86}Sr$ = 0.7098± 0.0008 (n=4, 2SD). SF L7 is unexpectedly high and it not known if such a value is reproducible in Sherwood Forest or other ancient woodlands in Britain. The woodland effect and it implications for archaeological studies is further discussed in section 8.2.

The Silurian sedimentary bedrock within the Welsh Borderlands Fault System is an interesting area. The radiogenic plant values found on the outskirts of the Precambrian Longmyndian bedrock are in the north section of the fault system (chapter 4, section 4.4), with the Silurian bedrock being in fault contact with the older Precambrian lithologies (Greig *et al*., 1968, p.2-3, 141-144; Toghill, 1990, p.92-94, 96). The Silurian bedrock mainly dates to the Ludlow and consists of a variety of undifferentiated mud-, silt- and sandstones (Woodcock & Pauley, 1989; BGS, 2004, Sheet 197). Currently, there is one water sample (JMW_05: Montgomery *et al.,* 2006) and six plant samples (USK-01, -02, -03, -04 and SHC L1 and L5: Evans *pers.com.*; chapter 4, section 4.6) on these Silurian rocks. Together they have biosphere $^{87}Sr/^{86}Sr$ = 0.7135 ±0.0040 (n=7, 2SD). Out of the seven samples only two have $^{87}Sr/^{86}Sr$ values <0.713, USK-01 at 0.71012 and USK-03 at 0.71230 (Evans, *pers.com*.). A further two of the plant samples are also taken from ancient woodland, USK-04 at 0.71550 (Evans, *pers.com*.) and SHC L5 at 0.71613 (chapter 4, section 4.6 and chapter 6). This is the only area in England and Wales at present that has the potential to be defined as highly radiogenic relative to the British biosphere in general, but more biosphere samples are needed to confirm this and they are not expected to be as high as seen in Scotland, with a possible maximum of ~0.716.

The last five plant samples with elevated values >0.714 are found across the Malvern Hills. They are either based on or believed to be influenced by the igneous rocks of the Precambrian Malvern Complex (G-V-023 and G-V-024G-V-026, G-V-030, S-WALES 02, Table 2.1: Chenery *et al.,* 2010; Evans, unpublished results; *pers.com*.). The plant$^{87}Sr/^{86}Sr$ at 0.71622 (G-V-026; Chenery *et al.,* 2010) is maximum value the Malvern Hills biosphere can produce currently. None of the high values were reproducible by the mixed plant samples collected across the Malvern Hills in this thesis (chapter 4, section4.2), with the highest plant $^{87}Sr/^{86}Sr$ at 0.71310 (MB10 A), 0.71321(MB10 B), 0.71346 (MB9 A) and 0.71347 (MB9 B). All of these samples are on the igneous rocks of the Precambrian Malvern Complex. Together, the Precambrian Malvern Complex have biosphere $^{87}Sr/^{86}Sr$ = 0.7133 ±0.0031 (n=11, 2SD: Montgomery *et al.,* 2006; Chenery *et al.,* 2010; Evans, unpublished results; *pers.com*.; chapter 4, section 4.2).

Overall, the maximum plant $^{87}Sr/^{86}Sr$ = 0.716 for England and Wales, while the maximum water $^{87}Sr/^{86}Sr$= 0.715.

8.1.2. The radiogenic nature of thermal/metamorphic aureoles

Two study areas within this thesis have produced aureoles of high biosphere $^{87}Sr/^{86}Sr$ values >0.714 around the base of mountains or hills; the Long Mynd and Stretton Hills near Church Stretton (chapter 4, section 4.4.3.1) and the Geal-charn Mor and Cairngorms mountains in central Scotland (chapter 5, section 5.4.1).

A aureole with elevated biosphere $^{87}Sr/^{86}Sr$ values was first suggested in Evans *et al.* (2009), where the plant biosphere surrounding the granitic Red Hills of the Isle of Skye gave values of 0.7165–0.7199, although the surrounding bedrock is predominantly limestone or basalt. Evans *et al.,* (2009) state that this highlights the topographic effect of the mountains, where the increased weathering and erosion from the mountains has masked the surrounding land. These more radiogenic plant values are within ~3km of the Red Hills to the south-east and ~4km to the north-west. If all the biosphere samples within ~4km of the Red Hills, which includes four samples between 0.709-0.710 to the south-east, have a mean $^{87}Sr/^{86}Sr$ = 0.7144 ± 0.0093 (n=9, 2SD: calculated from data in Evans *et al.,* 2009). If the four samples between 0.709 - 0.710 are excluded, the mean becomes 0.7182 ±0.0026 (n=5, 2SD). A plant sample growing on the granitic rocks of the Red Hills has $^{87}Sr/^{86}Sr$ = 0.71007 (Skye 17p), which is an approximate difference of -0.003 minimum compared to the aureole of $^{87}Sr/^{86}Sr$ values around the mountains base. However, this plant sample was taken near the coast and so is likely influenced by marine Sr and may not reflect the overall $^{87}Sr/^{86}Sr$ on these granitic rocks (Evans *et al.,* 2009).

Interestingly, all the elevated $^{87}Sr/^{86}Sr$ values >0.714 approximately north of the Silurian Monadhliath and Cairngorm Plutons in central Scotland, are also within ~4km distance. The plutons have biosphere $^{87}Sr/^{86}Sr$ = 0.7156 ±0.0022 (n=5, 2SD: chapter 5, section 5.4.1; Evans *et al.,* 2010), while the plant $^{87}Sr/^{86}Sr$ = 0.7174 ±0.0049 (n=7, 2SD: chapter 5, section 5.4.1) around the base of the plutons, which is a difference of +0.0018 between the surround base and the plutons. The Precambrian bedrock of the Long Mynd and Stretton Hills, near Church Stretton, have plant $^{87}Sr/^{86}Sr$ = 0.7116 ±0.0003 (n=5, 2SD: chapter 4, section 4.4.4). All the mixed plant samples within approximately 4km of the Precambrian inliers, regardless of the bedrock geology, have $^{87}Sr/^{86}Sr$ = 0.7137 ±0.0027 (n=7, 2SD), which is an average difference of +0.0021 compared to the plant $^{87}Sr/^{86}Sr$ on the Long Mynd and Stretton Hills.

So far the common trends for these aureoles of elevated $^{87}Sr/^{86}Sr$ values are that they are in close contact to large igneous intrusions or very old, Precambrian inliers and that they can be elevated by approximately +0.002 or greater compared to the biosphere $^{87}Sr/^{86}Sr$ of the bedrock lithologies they surround.

8.1.2.1. Thermal aureoles or weathering aureoles?

Evans *et al.,* (2009) note how the topographic effect of the Red Hills in the Isle of Sky have possibly increased the weathering and erosion of the granitic bedrock, masking the surrounding land at lower elevations. However, a common trend between the biosphere aureoles in the Isle of Skye and the Cairngorm National Park in Scotland is not just that they form around mountains, but large granitic intrusions (>10km wide).

Intrusive igneous bodies such as these provided a heat source for extensive hydrothermal activity during their emplacement and create a thermal, or metamorphic, aureole. This is where the country rock immediately in contact with the intrusion is altered by contact metamorphism to produce new metamorphic rocks and the resulting rocks are often enriched in polymetallic mineralisation because of the hydrothermal activity. The geochemical modelling of the soils on and around the Variscan granite intrusions of south-west England by Kirkwood *et al.* (2016),demonstrate that the concentration of Tin (Sn) in the soil is strongly controlled by hydrothermal mineralisation (Figure 8.1). This has resulted in Sn becoming concentrated in close proximity to the granite intrusions. Rubdium (Rb) is another element that is hydrothermally mobile and acts in a similar way to Sn. Figure 8.2 displays the concentration of Rb in the soil around the Variscan granite intrusions and again is highly concentrated in close proximity to the granite intrusions. The importance of Rb being hydrothermally mobile is that the radioactive isotope ^{87}Rb decays into ^{87}Sr (chapter 2, section 2.1), so where Rb concentrates so does the potential for ^{87}Sr, which in turn can result in higher ^{87}Sr/^{86}Sr that can be released into the biosphere.

Another observation is that the high concentrations of Sn and Rb in the soils around the Variscan granite intrusions also seem to be within 5km of the intrusions and are not evenly spread, concentrating mainly on the southern side of intrusion (Figure 8.1 and 8.2). Similar trends are seen in the biosphere ^{87}Sr/^{86}Sr data for the aureoles of the Red Hills (Isle of Skye), where the highest values are to the north-west and lower values to the south-east. The plant ^{87}Sr/^{86}Sr have not been collected evenly around the plutons in the Cairngorms National Park (Scotland: chapter 5, Figure 5.1), but from plant ^{87}Sr/^{86}Sr available, the highest values tend to lie to the north on the Precambrian Grampian Group which is in contact with the Silurian Cairngorm Pluton. All the plant samples within 5km of the Glen Gairn, Ballater and Lochnagar Plutons have ^{87}Sr/^{86}Sr = 0.7121 ±0.0029 (n=7, 2SD: based on results in chapter 5, section 5.3). These samples are more reflective of the bedrock geology they are taken from (chapter 5, section 5.3 and 5.4) and so could reflect the uneven influence of the thermal aureoles, but further biosphere ^{87}Sr/^{86}Sr is needed to define this.

The high plant ^{87}Sr/^{86}Sr seen around the Precambrian inliers of the Long Mynd and Stretton Hills near Church Stretton are more difficult to explain. In chapter 4, section 4.4, the elevated plant ^{87}Sr/^{86}Sr that form an aureole around the Precambrian inliers were suggested to be a result of weathering, possibly due to the repeated motion of glaciers advancing and retreating during the last glacial maximum. However, in light of the trends seen between thermal aureoles and radiogenic ^{87}Sr/^{86}Sr above, perhaps the Ordovician granite intrusion approximately 5-10km under the surface (Toghill, 1990, p.75-77) is having more influence than expected.

Hydrothermal fluids caused by the thermal aureole of a igneous intrusion can commonly travel along faults and form hydrothermal mineral deposits, where hydrothermally mobile elements, such as Rb, can concentrate. Areas where Rb concentrates can potentially result in higher ^{87}Sr/^{86}Sr. The older Precambrian and

Cambrian bedrocks in the Church Stretton district are also cut by many igneous intrusions dating to the late Ordovician and are possibly linked to the granite intrusion underground (Greig *et al.,* 1968, p.53), which again may produce higher $^{87}Sr/^{86}Sr$ in the biosphere. Referring back to Figure 4.4.1 in chapter 4, section 4.4, one of the radiogenic plant values >0.714 is on the felsic igneous tuffs of the Ordovician (CS L2), another may be a result of the many igneous dykes that intrude into the Precambrian Longmyndian (CS L3) and the final one is near to the fault zones of the Church Stretton Fault System (CS L12), along with another plant sample to the north that records $^{87}Sr/^{86}Sr$ at 0.71374 (CS L6). However, several other plants samples near the Church Stretton Fault Systems record $^{87}Sr/^{86}Sr$ between 0.711 -0.712, so the above hypothesis does not fully explain these elevated values.

Although the reasons behind these Sr-isotope biosphere aureoles with high $^{87}Sr/^{86}Sr$ values may not be fully defined at present, their greatest importance comes in the fact that values >0.714 can occur at elevations that are suitable for arable farming and the grazing of larger domestic animals, such as cattle. When $^{87}Sr/^{86}Sr$ values >0.714 are recorded by archaeological humans and animals outside of Scandinavia in Europe, they are often interpreted simplistically as being from the consumption of crops grown on ancient or granitic rocks (Jay *et al.,* 2007; Evans *et al.,* 2012; Parker Pearson *et al.,* 2016; Montgomery, *pers.com*.). A lot of the ancient or granitic terrains in Europe are mountainous, with poor, acidic soils that can become saturated in rainwater, which can lead to lower $^{87}Sr/^{86}Sr$ values in the biosphere. They are usually unattractive to farmers and rather than the assumption that people are trying cultivate crops or graze cattle on these mountain sides, these biosphere aureoles provide evidence for how these people and animals could be obtaining their high $^{87}Sr/^{86}Sr$, at elevations suitable for agricultural practices.

8.1.3. Sr-isotope biospheres on the quartzite formations of the Precambrian Dalradian Supergroup

Apart from on and around the Cairngorms suite (see section 8.1.1.1), all other plant sample with $^{87}Sr/^{86}Sr$ >0.714 across the Cairngorms National Park in Scotland, are sporadic, occurring alongside lower values, e.g. <0.713. A common trend between these sporadic values >0.714, are that they are located on the Precambrian quartzite formations of the Dalradian Supergroup (chapter 5, section 5.4.2). Only Evans *et al.* (2010) and chapter 5 within this thesis have collected plant samples from these quartzite formations. Together they have plant $^{87}Sr/^{86}Sr$ = 0.7139 ±0.0027 (n=8, 2SD).

Two of the plant samples, EBP-12 and EBP-22 (Evans *et al.,* 2010) are both located within approximately 20km of the coast and so may have some marine influence. If they are excluded, the plant $^{87}Sr/^{86}Sr$ = 0.7144 ±0.0021 (n=6, 2SD) instead. However, the plant sample SCOT L11, at 0.71292, located in the centre of the Cairngorms National Park, is over 75km away from the nearest coastline and is amongst the more radiogenic values based on the quartzite formations. Therefore the range of $^{87}Sr/^{86}Sr$ seen at present most likely reflects the heterogeneous nature of this lithology.

To characterize the biosphere $^{87}Sr/^{86}Sr$ of the Precambrian quartzite formations further, sampling from the following areas is recommended: the north of the village of Tomintoul, on the large Knockando Quartzite Formation (Grampian Group: BGS, 1997, Solid Geology, Sheet 85W); on the An Socach Quartzite Formation (Appin Group: BGS, 2008, Bedrock, Sheet 64E) towards the town of Blair Atholl (Perthshire); further south-west approximately 70km, near the village of Crianlarich (Perthshire), on the Carn Mairg Quartzite Formation (Argyll Group: BGS, 2013, Bedrock, Sheet 46W) and Glencoe Quartzite (Appin Group: BGS, 1992, Solid Geology, Sheet 45E). The best Sr-isotope package to use to represent the Precambrian quartzite formations of the Dalradian Supergroup in the Grampian terrane, Scotland, is the pink package with $^{87}Sr/^{86}Sr$ = 0.713 - 0.720 (Evans *et al.* 2010).

8.1.4. The $^{87}Sr/^{86}Sr$ of plants directly rooted in exposed rock

All the plant samples currently known to be directly rooted in exposed bedrock are displayed in Table 8.2. The other known biosphere $^{87}Sr/^{86}Sr$ taken from the same bedrock lithology are also displayed in the table for comparison. It is believed that these plants have had access to any bioavailable Sr from the mineral decomposition of the rock they are rooted in, resulting in a higher $^{87}Sr/^{86}Sr$. The exception is plant sample SCOT L24 (shown in italic in Table 8.2), which is located on one of the Precambrian quartzite formations of the Dalradian Supergroup (discussed in section 8.1.3 above). The value from SCOT L24 showed no recognisable difference to others plant samples taken from the quartzite formations, despite being rooted in the exposed bedrock.

The plant samples CHW 06 and CHW 13 from Charnwood Forest are both only approximately +0.0006 more radiogenic than other plant samples taken from similar Precambrian lithologies, which is not a significant change in the $^{87}Sr/^{86}Sr$ value (a significant change is usually +0.001 or greater, see chapter 2, section 2.2). However, all the other plant samples in Table 8.2 have significant differences. The sample LD L8, on the Eskdale Pluton has a difference of +0.0017, while FOD L3 on Carboniferous Coal Measures, and JMPD_08 (NIGL, unpublished) on the Carboniferous Millstone Grit, both have differences +0.003 minimum. These values are not typical of the biosphere $^{87}Sr/^{86}Sr$ on their respective bedrock, but they are an interesting observation and do highlight a previously unrecognised way in which high $^{87}Sr/^{86}Sr$ >0.714 could be obtained.

It is not known how many of the plant samples with $^{87}Sr/^{86}Sr$ >0.714 in Table 2.1 (chapter 2, section 2.3.1) could be a result of plants being directly rooted in exposed rock or extremely thin soils as this has not previously been recorded during their collection. It is also very unlikely that humans and animals will specifically eat only plants grown in exposed rock and therefore acquire a more radiogenic value than typically displayed by the local biosphere. The discussion of chapter 7 (section 7.6.1) showed that even the ingestion of rock grit by a human often produces a bioaccessible value similar to seen naturally in the biosphere and not of these rare, rock-rooted plants. Even then, rock grit is very rarely consumed in enough quantity to significantly change the human $^{87}Sr/^{86}Sr$ (section 7.6.2) and it is likely to be the same for these rock-rooted plants. The consumption of rock-rooted plants should not be seen as a concern for migration and mobility studies.

8.2. Can a home be found in Britain for people with high $^{87}Sr/^{86}Sr$?

All of the archaeological humans excavated in Britain with enamel $^{87}Sr/^{86}Sr$ values >0.713 are displayed in Table 8.3. Those from Ferry Fryston (Yorkshire, England) had their $^{87}Sr/^{86}Sr$ estimated from Figure 186 in Jay *et al.* (2007, p.352) and their oxygen isotope values converted from $\delta^{18}O_{precip}$ (‰) to $\delta^{18}O$‰ (VSMOW) using equation 4 in Longinelli (1984). . Those from the Beaker People Project (BBP)have had their $^{87}Sr/^{86}Sr$ estimated from Figure 6 in Parker Pearson *et al.* (2016, p.630) and a summary table from Montgomery *et al.,* (forthcoming), both of which can be seen in Figure 8.3. All the archaeological humans who have $\delta^{18}O$‰ (VSMOW) values available are displayed alongside their $^{87}Sr/^{86}Sr$ in Figure 8.4. From Figure 8.4 there are a few people who do not have $\delta^{18}O$(VSMOW) values typical for Britain, but the majority do. Having such $\delta^{18}O$ (VSMOW) values does not mean these people definitely originated from Britain, as these values can also be found on the European continent.

The main areas where archaeological humans with values >0.713 have been excavated are in Neolithic sites in south-east Wales at Penywyrlod and Ty Isaf (Neil *et al.,* 2017), Bronze Age barrows in the Peak District (Parker Pearson *et al.,* 2016; Montgomery *et al.,* forthcoming), Iron Age sites at Ferry Fryston in West Yorkshire (Jay *et al.,* 2007) and the medieval cemetery at Hereford Cathedral (Evans *et al.,* 2012). There are also several Bronze Age humans (unspecified) with$^{87}Sr/^{86}Sr$ >0.713, included in the Beaker People Project from barrows located in north-east to south-east coast of Scotland and south-west England on the Cretaceous Chalk (Parker Pearson *et al.*, 2016; Montgomery *et al.,* forthcoming). Figure 1.2 in chapter 1 displays the burial locations of these main sites or areas in Britain.

Although oxygen isotope data is available for the archaeological humans in the Beaker People Project, this data is not in a format that can be matched to each individual's $^{87}Sr/^{86}Sr$ value (Parker Pearson *et al*., 2016; Pellegrini *et al*., 2016). Therefore the humans with $^{87}Sr/^{86}Sr$ >0.713 from the Beaker People Project are not displayed in Figure 8.4. Two humans within the Beaker People Project from the Peak District of England, have $^{87}Sr/^{86}Sr$ at approximately 0.7184 and 0.7190 (Table 8.3: Parker Pearson *et al.,* 2016). Their $^{87}Sr/^{86}Sr$ currently exceed the maximum plant $^{87}Sr/^{86}Sr$ of Britain, at ~0.716 for England and Wales and ~0.718 for Scotland (section 8.1.1) and so are likely not British. Even though the maximum water $^{87}Sr/^{86}Sr$ value for Scotland is ~0.720 (section

8.1.1.1), the maximum plant $^{87}Sr/^{86}Sr$ is used to define a cut off point for humans considered British, as plants are the dominant dietary input of Sr into humans (Burton & Wright, 1995; Montgomery, 2010). These maximum plant $^{87}Sr/^{86}Sr$ values for England and Wales and Scotland can also be applied to any enamel $^{87}Sr/^{86}Sr$ from animals, as their dominant dietary input of Sr also comes from plants.

Currently only Scotland produces biosphere $^{87}Sr/^{86}Sr$ values >0.716 consistently in Britain (section 8.1.1.1). The areas known to produce radiogenic biosphere values >0.716 include: the Silurian Cairngorm suite and the biosphere aureole to the north in the Cairngorms National Park (section 8.1.1.1, section 8.1.2.); around Lairg, Sutherland, based on Precambrian psammites of the Highland terrane (Evans *et al.,* 2010); biosphere aureole around the Tertiary granites on the Isle of Skye (Evans *et al.,* 2009). These are the only areas at present that humans excavated in Britain with $^{87}Sr/^{86}Sr$ values >0.716 could have originated from, if they are believed to have originated from Britain.

For archaeological humans with $^{87}Sr/^{86}Sr$ values between 0.713 - 0.716 in Britain, the Cairngorms National Park (section 8.1.1.1) in Scotland is still viable, as plant $^{87}Sr/^{86}Sr$ range from 0.71303 - 0.71820 (chapter 5, section 5.4.1), but so are the Precambrian Malvern Complex of the Malvern Hills (chapter 4, section 4.2) and the Silurian Ludlow sedimentary rocks along the Welsh Border, from the village of Boughrood (Powys, Wales) to the outskirts of the Precambrian Longmydnian bedrock near Church Stretton (section 8.1.1.2). The Lower Palaeozoic mudstones and shales in central Wales can also produce ground water $^{87}Sr/^{86}Sr$ up to 0.71521 and stream water up to 0.71448 (Shand *et al.,* 2007), but it is not known if plant $^{87}Sr/^{86}Sr$ from the same area will produce similar radiogenic values.

Altogether the areas with high biosphere $^{87}Sr/^{86}Sr$ >0.714 equate to approximately 2.8% of Britain and, with the exception of the biosphere aureole to the north in the Cairngorms National Park (section 8.1.1.1, section 8.1.2.) and a couple of locations on the Silurian Ludlow sedimentary rocks along the Welsh Border, the majority would currently be considered agriculturally marginally and not suitable for sustaining large archaeological populations reliant on arable farming. However, if the woodland effect can be further supported in the future, higher biosphere $^{87}Sr/^{86}Sr$ >0.714 may be found or interpreted at elevations more suitable and accessible for agriculture and archaeological populations in Britain.

8.2.1. Implications of the woodland effect

Chapter 6 has indicated that large (>1km^2) ancient woodlands on Triassic bedrock in England and Wales have the potential to increase plant $^{87}Sr/^{86}Sr$ by approximately +0.002. It is believed woodlands can alter the biosphere through the woodland effect and so should be seen as a separate domain compared to other plant samples taken from agricultural land, open grass land, heath land, moor land, etc. However, this study is preliminary and further work is needed to confirm if this trend is replicated elsewhere and to define the changes in plant $^{87}Sr/^{86}Sr$ in biospheres hosted by different bedrock lithologies. It is expected that woodlands will affect the plant $^{87}Sr/^{86}Sr$ greatest on lithologies where the carbonate minerals can be leached out over time, such as mudstones and shales, probably resulting in a difference of +0.002 or greater between woodland plant $^{87}Sr/^{86}Sr$ and agricultural land plant $^{87}Sr/^{86}Sr$. Limestone or chalk bedrock, consisting purely of carbonate minerals, will potentially show no difference between woodland and agricultural land plant $^{87}Sr/^{86}Sr$ because of their homogenous nature. It is currently hard to predict if any change will occur between woodland and agricultural land plant $^{87}Sr/^{86}Sr$ on igneous lithologies and their metamorphic equivalents, because they are predominantly made of silicate minerals which are more resistant to weathering processes such as leaching (Faure, 1986, p.183ff).

If such trends are also found in other ancient woodlands in Britain this could have major implications to how biosphere $^{87}Sr/^{86}Sr$ data are interpreted in migration and mobility studies, particularly from plant samples. Sherwood Forest provides a useful example of how biosphere data may vary in forested areas. The ancient woodland of Sherwood Forest used to cover an area approximately 10 times greater than what remains today (~40km^2 vs.~4km^2:Natural England, 2014; The Sherwood Forest Trust). During medieval Britain, Sherwood Forest alone covered approximately 20% of the Triassic Sherwood Sandstone Group (on the East Midlands Shelf) and can be assumed to have plant $^{87}Sr/^{86}Sr$ = 07144 ±0.0056 (n=3, 2SD: chapter 6). Any deforested areas used as agricultural land in the medieval period can also be assumed to have plant $^{87}Sr/^{86}Sr$ = 0.7096 ±0.0012 (n=10, 2SD: Evans *et al.,* 2010; Chenery *et al.,* 2011; section 6.4.1). Therefore medieval humans living in the region of Sherwood Forest could be expected to have $^{87}Sr/^{86}Sr$ that lies between the forest and the agricultural land biosphere values, if they obtained their childhood diet locally.

A medieval site at Repton (near to Derby), also on the Triassic Sherwood Sandstone Group similar to Sherwood Forest above, excavated humans with enamel $^{87}Sr/^{86}Sr$ between 0.70898 - 0.71200 (n=8: Budd *et al.,* 2004; Evans *et al.,* 2012). This site is historically documented as a camp and cemetery of the Great Viking Army (The Anglo Saxon Chronicle, 1912; Biddle & Kjølbye-Biddle, 2001) and so Viking migrants are expected. The previous estimation of the biosphere overlying Triassic bedrock in Britain have $^{87}Sr/^{86}Sr$ = 0.7097 ±0.0006 (n=54, 1SD), which is mainly based on water samples (Evans *et al.*, 2010). Using this previous estimation, interpretations of the human $^{87}Sr/^{86}Sr$ data from the medieval site at Repton would have lead to any of the humans with values >0.711 being defined as migrants to the area. However, in light of the plant $^{87}Sr/^{86}Sr$ data obtained in the course of this thesis all these people could be considered local to their burial environment. This is just a speculative example of how the woodland effect could alter interpretations of human $^{87}Sr/^{86}Sr$ values. The oxygen isotope data of the humans excavated from the medieval site at Repton, reported as $\delta^{18}O_{dw\ SMOW}$ (‰) using the calibration developed by Levinson *et al.* (1987), as well as other archaeological evidence, such as grave goods, indicate that there are Viking migrants at Repton (Biddle & Kjølbye-Biddle, 2001; Budd *et al.,* 2004).

The following examples considers the implications of the woodland effect through time in England and Wales, focusing particularly on the humans with $^{87}Sr/^{86}Sr$ >0.713 (Table 8.3) and are based on the following assumptions: any large (>1km^2) woodland on sedimentary bedrock will be differentiated by approximately +0.002 in the biosphere $^{87}Sr/^{86}Sr$, with the exception of limestone or chalk bedrock which will show no difference in biosphere values; any large (>1km^2) woodland on metamorphic bedrock derived from sedimentary rock in England and Wales will show a difference of approximately +0.002 in the biosphere values; woodlands on igneous bedrock and their metamorphic equivalents will show no difference in biosphere values; any areas heavily influenced by atmospheric or marine Sr (~0.7092: Veizer, 1989, p.142; Evans *et al*., 2009; Evans *et al.,* 2010) today have remained so through time; any areas of open grass land, moor or heath land, etc., have the same biosphere $^{87}Sr/^{86}Sr$ in the past as they record today.

Mesolithic- Neolithic

Any migration and mobility studies dating to the Neolithic will have to carefully consider the woodland effect in their interpretations of human $^{87}Sr/^{86}Sr$. A recent study by Neil *et al.* (2017) analysed individuals dating to the Neolithic at the sites of Ty Isaf and Penywyrlod in south Wales. The earlier site of Penywyrlod, which is believed to coincide with the appearance of agriculture in Wales, has human $^{87}Sr/^{86}Sr$ ranging from 0.71323 - 0.71702 (n=11), with two individuals with values >0.716, while the later site of Ty Isaf has human $^{87}Sr/^{86}Sr$ ranging from 0.71017 -0.71524 (n= 9). The Ty Isaf site also contained cattle remains, dating to the later Neolithic, with enamel $^{87}Sr/^{86}Sr$ at 0.71304 and 0.71312. The $\delta^{18}O$‰(VSMOW) of these Neolithic people, ranging from 17.1 -19.4, also compare well to the values expected from human enamel in higher rainfall areas in Britain, at 18.2‰ ±1.0 (n=40, 2SD: Evans *et al.,* 2012). Based on the biosphere $^{87}Sr/^{86}Sr$ available to the authors, everyone with $^{87}Sr/^{86}Sr$ up to 0.7137 at the two sites probably obtained their childhood diet locally, as the local biosphere $^{87}Sr/^{86}Sr$ = 0.7097 - 0.7137 within ~16km of the sites, which is based mainly on the Lower Devonian sedimentary bedrock. The biosphere value at 0.7137, from an Ivy plant (S-Wales 42; Table 3 in Neil *et al.,* 2016, p.12), is a lone occurrence and the average local biosphere $^{87}Sr/^{86}Sr$ = 0.7107 ±0.0010 (n= 12, 1SD) for the sites of Ty Isaf and Penywyrlod.

In the Neolithic, when woodlands are assumed to be much more extensive than today in Wales, the biosphere $^{87}Sr/^{86}Sr$ on the sedimentary rocks of the Devonian (excluding the limestone lithologies) could be expected to have values +0.002 higher, so the biosphere range becomes 0.7097 - 0.7157 approximately. For example, two plant samples currently taken from ancient woodland on Silurian Ludlow bedrock just over 20km to the north-west of these sites, have $^{87}Sr/^{86}Sr$ = 0.71550 (USK-04) and 0.71613 (SHC L5), which is approximately a difference of +0.002 compared to the highest values taken from agricultural land (at 0.71334, USK-02: chapter 6, section 6.5). If these Neolithic people were still obtaining a high proportion of their childhood diets from the woodlands their $^{87}Sr/^{86}Sr$ could be expected to be more radiogenic, perhaps ranging from 0.713 - 0.716. Therefore the majority of the Penywyrlod population could either be interpreted as migrants to the area, or obtaining their childhood diets from the woodlands, with the exception of the individual with $^{87}Sr/^{86}Sr$ = 0.71702 who currently exceeds all current known biosphere $^{87}Sr/^{86}Sr$ data in Wales. Neil *et al.* (2017) radiocarbon dated this individual to the first few centuries of the 4th millennium BC, consistent with the period when agriculture was initiated in Wales. The authors originally suggested values >0.717 are only presently seen in Scotland in Britain, but they further explain how current Bayesian modelling suggests this individual coincides with the first appearance of

Neolithic material culture in Scotland, making migration from such a place in the time scale available difficult to explain. This individual can be considered a migrant to Britain and possible origins include Lower Normandy, Brittany and Pays de la Loire in north-western France (Neil *et al.* 2017) and also the Central Massif in France, based on the Sr-isotope biosphere map of France produced by Willmes *et al.* (2014)(described previously in chapter 2, section 2.4.2).

The population from Ty Isaf post dates the first appearance of agriculture in Wales (Neil *et al.,* 2017) and has $^{87}Sr/^{86}Sr$ that may reflect their agricultural practices, which inevitably involved deforestation resulting in a lowering of the $^{87}Sr/^{86}Sr$ in the biosphere. The cattle and the people with higher $^{87}Sr/^{86}Sr$ >0.713 again may have obtained a large proportion of their diet from woodland. The grazing of domesticated animals such as cattle and pigs in forests is believed to have occurred since the Neolithic (Rowley-Conwy, 1987; Brown, 1997; Robinson, 2000a,b) as well as the feeding of leaf fodder to stalled animals (Bell & Walker, 2005, p.164-168). The difference in human $^{87}Sr/^{86}Sr$ values between these two Neolithic sites is interesting, but the woodland effect, if valid, might make their interpretations more complicated.

Neolithic - Iron Age

By the Iron Age it has been estimated that 50% of woodland in England had been lost (Bell & Walker, 2005, p.164-168). Any area that still had large (>1km^2) woodlands present throughout the Neolithic to the Iron Age will probably have Sr-isotope biospheres that have been influenced by the woodland effect. The problem that will arise here is knowing whether these woodlands were still extensive locally to the study site. Environmental evidence may have to be relied on to decide if this is the case.

Several Bronze Age and Iron Age humans with $^{87}Sr/^{86}Sr$ between 0.713 - 0.717 (Table 8.3, Figure 1.2 in chapter 1) have been excavated from sites overlying the Carboniferous Dolomitised Limestones of central England. They include seven Bronze Age individuals from the Peak District, all belonging to the Beaker People Project (Parker Pearson *et al*., 2016; Montgomery *et al.,* forthcoming), and the six Iron Age individuals from Ferry Fryston, West Yorkshire (Jay *et al.,* 2007). The remains of two cows from the Iron Age chariot burial at Ferry Fryston have also produced radiogenic $^{87}Sr/^{86}Sr$, at approximately 0.715 (cattle 5) and 0.720 (cattle 3)(Jay *et al.,* 2007). The Carboniferous Dolomitised Limestones have biosphere $^{87}Sr/^{86}Sr$ = 0.7092 ±0.0004 (n=11, 2SD: Evans *et* *al.*, 2010), while the nearby Carboniferous Millstone Grits have biosphere $^{87}Sr/^{86}Sr$ = 0.7113 ±0.0016 (n=9, 2SD: Evans *et al.,* 2010; NIGL, unpublished). Any large woodlands (>1km^2) on the limestone lithologies are not expected to produce higher biosphere $^{87}Sr/^{86}Sr$ because of the woodland effect, but woodlands on the Millstone Grits could be +0.002 higher than expected, resulting in possible values between 0.7133 ±0.0016 (2SD). Even with the estimations of the woodland effect, the highest biosphere values on the Millstone Grit may only be ~0.714, meaning the majority of the humans and cattle with $^{87}Sr/^{86}Sr$ >0.714 from the Peak District and Ferry Fryston can still be considered migrants to their burial locations.

One human from the Peak District and two humans from Ferry Fryston have $^{87}Sr/^{86}Sr$ values >0.716 (Table 8.3). These people have $^{87}Sr/^{86}Sr$ values that can only currently be found in the radiogenic biospheres of Scotland (section 8.1.1.1). As for the rest of the humans, and cattle 5, with $^{87}Sr/^{86}Sr$ values between 0.714 -0.716 from Ferry Fryston, they can either originate from the same biospheres in Scotland (as the biosphere $^{87}Sr/^{86}Sr$ can range from 0.713-0.718), or from the Malvern Hills, the Lower Palaeozoic of central Wales or the Silurian Ludlow bedrock of the Welsh Border, if they are considered British. Other potential areas outside of Britain such as Lower Normandy, Brittany, Pays de la Loire and the Central Massif in France (Willmes *et al.*,2014) could all still be viable areas of origin. Cattle 3 has an $^{87}Sr/^{86}Sr$ value, at 0.720 (Jay *et al.,* 2007), that currently exceeds the maximum plant $^{87}Sr/^{86}Sr$ of Britain (section 8.1.1) and so is unlikely to be British. The only places that are known to produced biosphere $^{87}Sr/^{86}Sr$ values >0.720 are overlying the Central Massif in France (Willmes *et al.*,2014) and the Precambrian granites and gneisses of Scandinavia, mainly in Sweden (see chapter 2. Section 2.4.2).

<u>Roman Period onwards</u>

By the Roman period, lime had became a popular fertiliser in Britain (Goulding *et al.,* 1989; Goulding, 2016). The use of lime is expected to input $^{87}Sr/^{86}Sr$ values ~0.708-0.709 into the biosphere. These values are similar to the plant $^{87}Sr/^{86}Sr$ data from agricultural land on the Triassic Sherwood Sandstone Group (chapter 6, section 6.4.1). However, all the water samples currently from Triassic bedrock also have $^{87}Sr/^{86}Sr$ = 0.7097 ±0.0010 (n=21, 2SD: Spiro *et al.,* 2001; Montgomery *et al.,* 2006; Evans *et al.,* 2010). As the majority of these water samples are from aquifers or mineral waters, they are assumed to have homogenised well with the Triassic bedrock and are free of modern pollutants. They essentially show what the biosphere $^{87}Sr/^{86}Sr$ on the Triassic bedrock can produce without the influence of the woodland effect or fertilisers. The problem is that the water $^{87}Sr/^{86}Sr$ on the Triassic bedrock and the $^{87}Sr/^{86}Sr$ of the lime fertiliser are similar and so the addition of lime across agricultural land on Triassic bedrock is not expected to be distinguishable in the biosphere $^{87}Sr/^{86}Sr$. For other sedimentary bedrock (excluding limestone and chalk) in England and Wales, the addition of lime may have resulted in a larger difference between the biosphere $^{87}Sr/^{86}Sr$ of agricultural land and the biosphere $^{87}Sr/^{86}Sr$ of woodland on the same bedrock.

From the Roman period onwards, the use of fertilisers on agricultural land in Britain should be seen as a common practice. The validation of modern proxy data in Evans *et al.* (2010) have been compared to diagenetically altered bone and dentine values from post-Roman human and animals. It is possible that these bone and dentine $^{87}Sr/^{86}Sr$ values may have diagenetically altered to ancient pore fluids that have already been influenced by fertilisers, such as lime, and deforestation. Therefore modern biosphere proxy samples can be inferred back to at least the Roman period successfully, e.g. agricultural land in the Roman period and onwards can be assumed to have the same biosphere $^{87}Sr/^{86}Sr$ as recorded by agricultural land today.

There are not many humans with $^{87}Sr/^{86}Sr$ >0.713 buried in Britain date to the Roman period (Table 8.3). The majority are buried in York or within Yorkshire and their $^{87}Sr/^{86}Sr$ range between 0.713 - 0.714. York is mainly on the Triassic Sherwood Sandstone Group, while the whole of Yorkshire mainly consists of the Carboniferous Coal Measures, Millstone Grits and Dolomitised Limestones, Triassic Sherwood Sandstone Group and Cretaceous Chalk. Together, these lithologies can have biosphere $^{87}Sr/^{86}Sr$ that range from 0.708 - 0.713 (Evans *et al.,* 2010; Chenery *et al.,* 2011; Warham, 2011, p.125). The woodland effect may have resulted in woodland biosphere $^{87}Sr/^{86}Sr$ on the Carboniferous Coal Measures and Millstone Grits and the Triassic Sherwood Sandstone Group being +0.002 higher in value than the biosphere $^{87}Sr/^{86}Sr$ from agricultural land on the same bedrock. Therefore the Romans with $^{87}Sr/^{86}Sr$ between 0.713 -0.714 could either be migrants to York or have obtained their childhood diet from woodlands on the Sherwood Sandstone Group.

Four Roman cattle, with enamel $^{87}Sr/^{86}Sr$ = 0.71413 - 0.71582, have also been excavated from the Hive development site, Worcester. They have $\delta^{18}O$(VSMOW) typical for British cattle and are described as being advanced in age, so are assumed not have been able to travel great distances (e.g. unlikely to be transported from Europe) (Montgomery *et al.,* unpublished report). Worcester is on the Triassic Mercia Mudstone Group of the Worcester Basin, with biosphere $^{87}Sr/^{86}Sr$ = 0.7102 ±0.0017 (n=32, 2SD) (see section 8.3 below: Spiro *et al.,* 2001; Montgomery *et al.,* 2009; Chenery *et al.,* 2010; Evans, *pers.com*.; chapter 4, section 4.2). Any large woodlands (>1km^2) on this bedrock could be expected to produce biosphere $^{87}Sr/^{86}Sr$ = 0.7122 ±0.0017 (2SD), which could possibly explain the high $^{87}Sr/^{86}Sr$ >0.714 of these Roman cattle, if they were forest grazed or fed predominantly by leaf litter from the woodlands. The Malvern Hills are also within a~20km south of Worcester and the Silurian Ludlow bedrock in Wales is approximately 55km west, both of which currently produce biosphere $^{87}Sr/^{86}Sr$ >0.713 and maximum plant $^{87}Sr/^{86}Sr$ at ~0.716 (Chenery *et al.,* 2010; chapter 4, section 4.2; section 4.6). These cattle were unlikely to have originated from the Malvern Hills because the steep terrain is unsuitable for grazing cattle (Montgomery, *pers.com*.), but the Silurian Ludlow bedrock could potentially be from where these cattle originated. This bedrock has plenty of land suitable for grazing and arable farming and the maximum plant $^{87}Sr/^{86}Sr$ from the Silurian Ludlow bedrock are from ancient woodlands, so if these cattle were forest grazed they could have potentially obtained such radiogenic values through the woodland effect.

Finally, four humans buried in medieval Hereford (Evans *et al.,* 2012), with $^{87}Sr/^{86}Sr$ between 0.71302 - 0.71401 (Table 8.3), may also be a result of a diet based on local woodland vs. agricultural land. The local biosphere $^{87}Sr/^{86}Sr$ for the Devonian sedimentary bedrock, in which Hereford is based, is similar to reported in Neil *et al.* (2017) at 0.7097 - 0.7137, so the range could become 0.7097 - 0.7157 approximately if the woodland effect is valid. Therefore any values >0.713 could represent a diet obtained predominantly from large woodlands. Radnor Forest on the Silurian Ludlow bedrock, is also approximately 35km to the west of Hereford, and is known to produce plant $^{87}Sr/^{86}Sr$ up to 0.716 and so is another place of origin for these medieval humans from Hereford.

The humans and cattle of Neolithic Wales, Roman Worcester and medieval Hereford, with $^{87}Sr/^{86}Sr$ >0.713, strengthen the need for further biosphere sampling along the Welsh Border on the Silurian and Devonian bedrock, as it is here the maximum biosphere $^{87}Sr/^{86}Sr$ in England and Wales will potentially be defined, regardless of whether this is from agricultural land or woodland.

8.3. Defining other Sr-isotope biospheres in Britain: the Triassic

The majority of the study areas from central England (e.g. the Midlands) in this thesis have plant $^{87}Sr/^{86}Sr$ on Triassic bedrock. These study areas include: Charnwood Forest (chapter 4, section 4.1); the Malvern Hills (chapter 4, section 4.2); Nuneaton (chapter 4, section 4.3); Sherwood Forest and Burbage woods (chapter 6). A common trend emerged where plant samples often produced higher $^{87}Sr/^{86}Sr$ than the Triassic biosphere $^{87}Sr/^{86}Sr$ reported in Evans *et al.,* (2010), at 0.7097 ±0.0006 (n=54, 1SD), which is mainly based on water samples.

8.3.1. Geological Summary of the Triassic bedrock in Britain

The Triassic bedrock in Britain was deposited in a series of fault-bounded basins when the part of the supercontinent Pangaea that is now England, was subsiding and breaking apart (Hounslow & Ruffell, 2006; Howard *et al.,* 2008; Carney, 2010). The majority of these Triassic basins were linked and can be seen in Figure 8.5 (adapted from Howard *et al.,* 2008). The Triassic bedrock in Britain is split into three lithostratigraphical groups: the Sherwood Sandstone Group, the Mercia Mudstone Group and the Penarth Group.

The Sherwood Sandstone Group is a thick sequence of predominantly red, yellow and brown sandstones. In the Midlands, pebbles are common within the sandstones, forming conglomerate beds, but these become rare northwards towards Lancashire and Yorkshire. The majority of the Sherwood Sandstone Group has fluvial origins, containing numerous fining-upward cycles, but aeolian units also occur and in the Midlands marine units occur in the upper part of the group. The Mercia Mudstone Group then overlies the Sherwood Sandstone Group and comprises of formations that are argillaceous in nature (containing lots of clay minerals). This group is dominated by red mudstones, often referred to as 'red beds', but also contains subordinate siltstones with thick halite-bearing units in some basinal areas. It is thought to be deposited through wind action in subaqeuous playas or inland sabkha environments(Warrington *et al.,* 1980, Howard *et al.,* 2008). In turn the Penarth Group overlies the Mercia Mudstone Group. The Penarth Group contains formations that are argillaceous, calcareous and locally arenaceous in nature and are predominantly of marine origin. Dark grey to black mudstones are the most dominant lithology, with subordinate limestones and sandstones. The Mercia Mudstone Group and Penarth Group are not displayed separately on the BGS Bedrock Geology 1:625 000 scale map of Britain (2007) and so will be considered together *sensu lato.*

8.3.2. Discussion of Triassic biosphere $^{87}Sr/^{86}Sr$ data: Sherwood Sandstone Group vs. Mercia Mudstone Group

All of the Triassic biosphere $^{87}Sr/^{86}Sr$ data available from England are displayed in Figure 8.6. In this figure the biosphere $^{87}Sr/^{86}Sr$ is split into their proxy types and shown as the Triassic as a whole and then split into the Sherwood Sandstone Group and Mercia Mudstone Group (including the Penarth Group *sensu lato*). The Triassic bedrock combined has a mean biosphere $^{87}Sr/^{86}Sr$ = 0.7106 ±0.0031 (n=76, 2SD), while based on proxy type are as follows: water $^{87}Sr/^{86}Sr$ = 0.7097 ±0.0010 (n=21, 2SD: Spiro *et al.,* 2001; Montgomery *et al.,* 2006; Evans *et al.,* 2010) excluding one elevated value at 0.71161 (SRA201: Spiro *et al.,* 2001); plant $^{87}Sr/^{86}Sr$ = 0.7109±0.0027 (n=43, 2SD: Chenery *et al.,* 2010; Evans *et al.,* 2010; Chenery *et al.,* 2011; NIGL, unpublished; chapter 4, section 4.1, 4.2.4.3; chapter 6) excluding two elevated values at 0.71546 (G-V-023:Chenery *et al.,* 2010) and 0.71757 (SF L3: chapter 6, section 6.4.1); bone/dentine $^{87}Sr/^{86}Sr$ = 0.7099 ±0.0012 (n=7, 2SD: Trickett, 2007; Leach *et al.,* 2009; Montgomery *et al.,* 2009; Evans *et al.,* 2010); soil leach $^{87}Sr/^{86}Sr$ = 0.71030 and 0.71153 (Riccall soil 1 and REP 2: Evans *et al.,* 2010). Excluding the soil leaches as only two samples are recorded, the plant samples have the highest mean $^{87}Sr/^{86}Sr$ and the largest standard deviation (2SD), which can encompass all other biosphere values on the Triassic.

If the two Triassic lithostratigraphical groups are compared, the Sherwood Sandstone Group has a mean biosphere $^{87}Sr/^{86}Sr$ = 0.7106 ±0.0037 (n= 26, 2SD) and the Mercia Mudstone Group has a mean biosphere $^{87}Sr/^{86}Sr$ = 0.7107 ±0.0027 (n=50, 2SD). As the proxy types have not been collected evenly over the Sherwood Sandstone Group and Mercia Mudstone Group comparing them is difficult. For example all the water $^{87}Sr/^{86}Sr$ currently available is only on the Mercia Mudstone Group. Therefore, only the mean plant and bone/dentine $^{87}Sr/^{86}Sr$ data can be compared (Figure 8.6). The plant $^{87}Sr/^{86}Sr$ = 0.7103 ±0.0026 (n=20, 2SD) for the Sherwood Sandstone Group, excluding one elevated value at 0.71757 (SF L3; chapter 6, Section 6.4.1), while the Mercia Mudstone Group have plant $^{87}Sr/^{86}Sr$ = 0.7115 ±0.0023 (n=23, 2SD), excluding one elevated value at 0.71546 (G-V-023:Chenery *et al.,* 2010). The bone/dentine $^{87}Sr/^{86}Sr$ = 0.7095 ±0.0005 (n=3, 2SD) for the Sherwood Sandstone Group and 0.7100 ±0.0014 (n=4, 2SD) for the Mercia Mudstone Group.

In both cases, the Mercia Mudstone Group has the highest mean value for plant and bone/dentine samples. The difference is not significant (e.g. +0.001 or greater) between the two lithostratigraphical groups for the bone/dentine samples, at +0.0005. The plant $^{87}Sr/^{86}Sr$ show a significant difference of +0.0013 between the two lithostratigraphical groups, but the standard deviations also show a significant overlap with one another (Figure 8.6). However, it possible that the position and different sediment supplies for the basins, where these lithostratigraphical groups were deposited during the Triassic, may be the influencing factor here. The majority of the biosphere $^{87}Sr/^{86}Sr$ for the Sherwood Sandstone Group comes from the East Midlands Shelf, while the majority of the biosphere $^{87}Sr/^{86}Sr$ for the Mercia Mudstone Group comes from the basins in central and western Midlands (Figure 8.5).

8.3.3. Discussion of Triassic biosphere $^{87}Sr/^{86}Sr$ data: the Triassic Basins

Biosphere $^{87}Sr/^{86}Sr$ data is only available overlying the Triassic Chestershire/West Lancashire Basins, the East Midlands Shelf, the Needwood Basin, the Hinckley Basin and Worcester/Knowle Basins. The position of these Triassic basins can be seen in Figure 8.5 and the biosphere $^{87}Sr/^{86}Sr$, split by basin and proxy type, can be seen in Figure 8.7, apart from the Needwood Basin which only has one plant sample available on the Sherwood Sandstone Group, with $^{87}Sr/^{86}Sr$ = 0.70992 (JMPD_04: NIGL, unpublished). The mean biosphere $^{87}Sr/^{86}Sr$ for the Triassic basins are as follows: Cheshire/West Lancashire Basins $^{87}Sr/^{86}Sr$ = 0.7102 ±0.0013 (n=5, 2SD: Evans *et al.,* 2010; NIGL, unpublished); East Midlands Shelf $^{87}Sr/^{86}Sr$ = 0.7102 ±0.0030 (n=19, 2SD: Leach *et al.,* 2009; Evans *et al.,* 2010; Chenery *et al.,* 2011; NIGL, unpublished; chapter 6), excluding one elevated value at 0.71757 (SF L3; chapter 6, Section 6.4.1); Hinckley Basin $^{87}Sr/^{86}Sr$ = 0.7113 ±0.0019 (n=16, 2SD: Montgomery *et al.,* 2006; Trickett, 2007; NIGL, unpublished; chapter 4, section 4.1 and 4.3; chapter 6); Worcester/Knowle Basins $^{87}Sr/^{86}Sr$ = 0.7103 ±0.0022 (n=33, 2SD:

Spiro *et al.,* 2001; Montgomery *et al.,* 2009; Chenery *et al.,* 2010; chapter 4, section 4.2), excluding one elevated value at 0.71546 (G-V-023:Chenery *et al.,* 2010).

Although the standard deviations show a lot of overlap, the difference between the mean biosphere $^{87}Sr/^{86}Sr$ of the different basins probably reflects their different sediment supplies during their deposition in the Triassic. At present, there is an east (East Midlands Shelf), central (Hinckley Basin) and west (Cheshire/West Lancashire, Worcester/Knowle Basins) trend in the biosphere data.

The Cheshire/West Lancashire and Worcester/Knowles Basins have similar biosphere $^{87}Sr/^{86}Sr$. Both these basins are located in western Midlands (Figure 8.5) and would be best displayed by the Sr-isotope package 0.710-0.711 (light green). However, the current number of samples between the basins should be considered (e.g. five and 32 respectively) as well as where the $^{87}Sr/^{86}Sr$ data lies (Figure 8.7). The analysis of more biosphere proxies from the Cheshire/West Lancashire Basins may change the mean biosphere $^{87}Sr/^{86}Sr$ currently recorded. As for the Worcester/Knowle Basins, there is an approximate difference of +0.0014 between the mean plant and water $^{87}Sr/^{86}Sr$. Why there is such a difference between plant and water $^{87}Sr/^{86}Sr$ is not fully understood. The water samples from Spiro *et al.* (2001) come from aquifers and so are expected to have homogenised well with the Triassic bedrock, particularly as the water $^{87}Sr/^{86}Sr$ have a smaller standard deviation. The plant samples on the other hand have been collected from the Triassic bedrock to the west of the Malvern Hills, in which the Precambrian Malvern Complex have biosphere $^{87}Sr/^{86}Sr$ = 0.7133 ±0.0031 (n=11 ,2SD: Montgomery *et al.,* 2006; Chenery *et al.,* 2010; Evans, unpublished results; chapter 4, section 4.2). These plant samples on the Triassic bedrock have not been collected from ancient woodland, so the woodland effect cannot account for their higher than expected $^{87}Sr/^{86}Sr$ values. Instead, the weathering and erosion of the Malvern Hills may have influenced the plant $^{87}Sr/^{86}Sr$ in this area, resulting in a higher mean and larger standard deviation. The collection of plant samples further north on the Worcester/Knowles Basins, away from the Malvern Hills, may provide evidence that the above interpretation is correct. Considering that plants are the dominant dietary source of Sr in humans and animals (Burton & Wright, 1995; Montgomery, 2010), any humans or animals who are considered local will have $^{87}Sr/^{86}Sr$ values similar to the plant $^{87}Sr/^{86}Sr$ data on the Triassic bedrock in the Worcester/Knowle Basins (Figure 8.7). For example, Anglo-Saxon humans from Wasperton (near to Coventry) on the Mercia Mudstone Group of the Knowle Basin, commonly have $^{87}Sr/^{86}Sr$ between 0.71009 - 0.71239 (n=20: Montgomery *et al.,* 2009; Evans *et al.,* 2012). Based on the Triassic plant $^{87}Sr/^{86}Sr$ data, these Anglo-Saxon humans can be interpreted as having obtained their childhood diet locally by their $^{87}Sr/^{86}Sr$ values. However, other archaeological and isotopic evidence needs to be taken into account before ultimately deciding if these people are local or not to their burial environment.

The East Midlands Shelf biosphere $^{87}Sr/^{86}Sr$ = 0.7102 ±0.0030 (n=19, 2SD), excluding one elevated value at 0.71757 (SF L3; chapter 6, section 6.4.1), known to be from the ancient woodland of Sherwood Forest Nature Reserve on the Triassic Sherwood Sandstone Group. If all known plant samples believed to be influenced by the woodland effect are excluded from the mean biosphere $^{87}Sr/^{86}Sr$, it becomes 0.7097 ±0.0011 (n=16, 2SD). Altogether, including SF L3 at 0.71757, the ancient woodlands on the Triassic East Midland Shelf have plant $^{87}Sr/^{86}Sr$ = 0.7143 ±0.0046 (n=4, 2SD: Chenery *et al.,* 2011; chapter 6, section 6.4.1). Any large ancient woodlands (>1km^2) should be considered as a separate domain on the Triassic bedrock of the East Midland Shelf. Therefore the overall East Midlands Shelf should be displayed by the Sr-isotope package 0.709-0.710 (bright green), while the Sherwood Forest Nature Reserve should be 0.713-0.720 (pink).

The Hinckley Basin has the highest biosphere mean, at 0.7114 ±0.0019 (n=16, 2SD) and has a difference of +0.0011 compared to the other mean biosphere $^{87}Sr/^{86}Sr$ of the other Triassic basins. Six out of the 13 plant samples on this basin were taken from ancient woodland, however they are not distinguishable from the remaining seven plant samples taken from agricultural land, potentially due to the small size or the age of the ancient woodland (e.g. <1km^2 and <400 years old approximately: chapter 6, section 6.4.2). The difference in the mean biosphere $^{87}Sr/^{86}Sr$ value on the Hinckley Basin is potentially caused by a difference in sediment supply during the formation of the lithologies within the basin. Hinckley Basin should be displayed by the Sr-isotope package 0.711-0.712 (yellow).

The collection of more plant samples overlying the Triassic bedrock may result in a broader range of $^{87}Sr/^{86}Sr$ being expected from these lithologies in Britain. It would be interesting to see if further biosphere $^{87}Sr/^{86}Sr$ data on the Triassic basins continued to show different mean values from across east to west Britain.

8. Tables and Figures

Table 8.1. All of the radiogenic $^{87}Sr/^{86}Sr$ values >0.714 from within this thesis, along with short description of sample type, location, bedrock lithology and position coordinates.

Sample Code	**Sample type**	**Location**	$^{87}Sr/^{86}Sr$	**Bedrock Lithology**	**Longitude**	**Latitude**
SCOT GL3	Mixed Plant	Near Glenmore, Cairngorms National Park, Scotland	0.71820	Precambrian Meta-sediments	3 40 25.94W	57 09 55.26N
SCOT L23	Mixed Plant	Near Tomintoul, Moray, Scotland	0.71773	Precambrian Meta-sediments	3 26 18.1032W	57 16 19.7148N
SF L3	Mixed Plant	Sherwood Forest Nature Reserve, Nottinghamshire, England	0.71757	Triassic Sedimentary rocks	1 05 8.82W	53 12 28.51N
SCOT GL2	Mixed Plant	Near Glenmore, Cairngorms National Park, Scotland	0.71671	Precambrian Meta-sediments	3 46 05.08W	57 10 06.25N
SCOT CTL2	Mixed Plant	Near Chapeltown, Ballindalloch, Scotland	0.71656	Devonian Sedimentary rocks	57 16 30.83N	3 19 07.40W
SCOT GL8	Mixed Plant	Near Aviemore, Cairngorms National Park, Scotland	0.716394	Silurian Granitic rocks	3 55 06.45W	57 08 15.98N
SHC L5	Mixed Plant	Near to New Radnor, Kington, England	0.71613	Silurian Sedimentary rocks	3 08 57.6W	52 14 07.32N
FOD L3	Mixed Plant (rooted in exposed rock)	Great Berry Quarry, Brierley, Forest of Dean, England	0.71580	Carboniferous Sedimentary rocks	2 33 25.3W	51 49 52.7N
SCOT GL6	Mixed Plant	Near Aviemore, Cairngorms National Park, Scotland	0.71556	Precambrian Meta-sediments	3 49 28.14W	57 09 18.45N

Sample Code	Sample type	Location	$^{87}Sr/^{86}Sr$	Bedrock Lithology	Longitude	Latitude
SCOT L13	Mixed Plant	Near Braemar, Cairngorms National Park, Scotland	0.71555	Silurian Granitic rocks	3 19 33.68W	57 00 07.19N
CS L12	Mixed Plant	Near Church Stretton, Shropshire, England	0.71536	Ordovician Sedimentary rocks	2 48 51.6W	52 30 14.9N
CS L3	Mixed Plant	Near Church Stretton, Shropshire, England	0.71524	Precambrian Sedimentary rocks	2 54 45.5W	52 32 19.5N
SCOT L16	Mixed Plant	Near Ballater, Cairngorms National Park, Scotland	0.71487	Silurian Granitic rocks	3 01 27.20W	57 03 09.51N
LD L8	Mixed Plant (rooted in exposed rock)	Beckfoot Quarry, Lake District, England	0.71471	Ordovician Granitic rocks	03 17 23W	54 23 28N
SCOT L21	Mixed Plant	Near Tomintoul, Moray, Scotland	0.71465	Precambrian Meta-sediments	3 15 58.26W	57 13 6.10N
SCOT L25	Mixed Plant	Near Grantown-on-Spey, Moray, Scotland	0.71463	Ordovician Granitic rocks	3 37 33.81W	57 20 6.86N
SCOT L10	Mixed Plant	Near Braemar, Cairngorms National Park, Scotland	0.71432	Precambrian Quartzite	3 25 00.6276W	56 55 54.714N
SCOT CTL5	Mixed Plant	Near Chapeltown, Ballindalloch, Scotland	0.71426	Precambrian Quartzite	3 17 35.28W	57 17 41.07N
SCOT L24	Mixed Plant (rooted in exposed rock)	Near Grantown-on-Spey, Moray, Scotland	0.71418	Precambrian Quartzite	3 32 58.7112W	57 16 27.5088N
CS L2	Mixed Plant	Near Church Stroke, Powys, Wales	0.71406	Ordovician Felsic tuffs	3 00 22.1W	52 32 33.7N

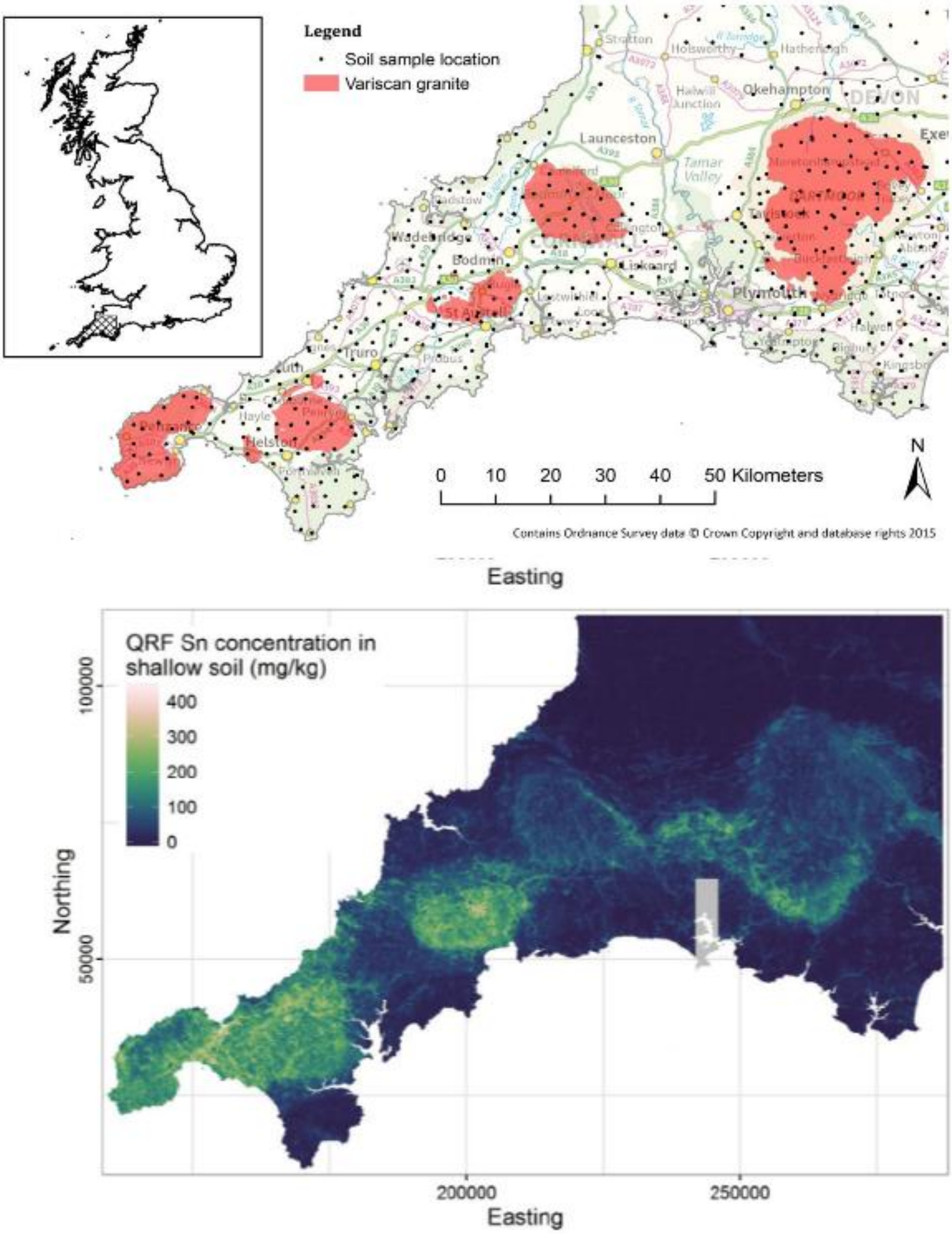


Figure 8.1.Figure 1 (above) and 4 (below) from Kirkwood *et al.* (2016). The top map displays the locations of 2012 field season G-BASE soil samples within the study area in southwest England. The inset map shows the study area (cross-hatched) in reference to the rest of Great Britain, along with the positions of the Variscan granitic intrusions as they are prominent geological and geochemical landmarks within the region. The bottom map displays the quantile regression forest predicted concentration for Sn in shallow soils.

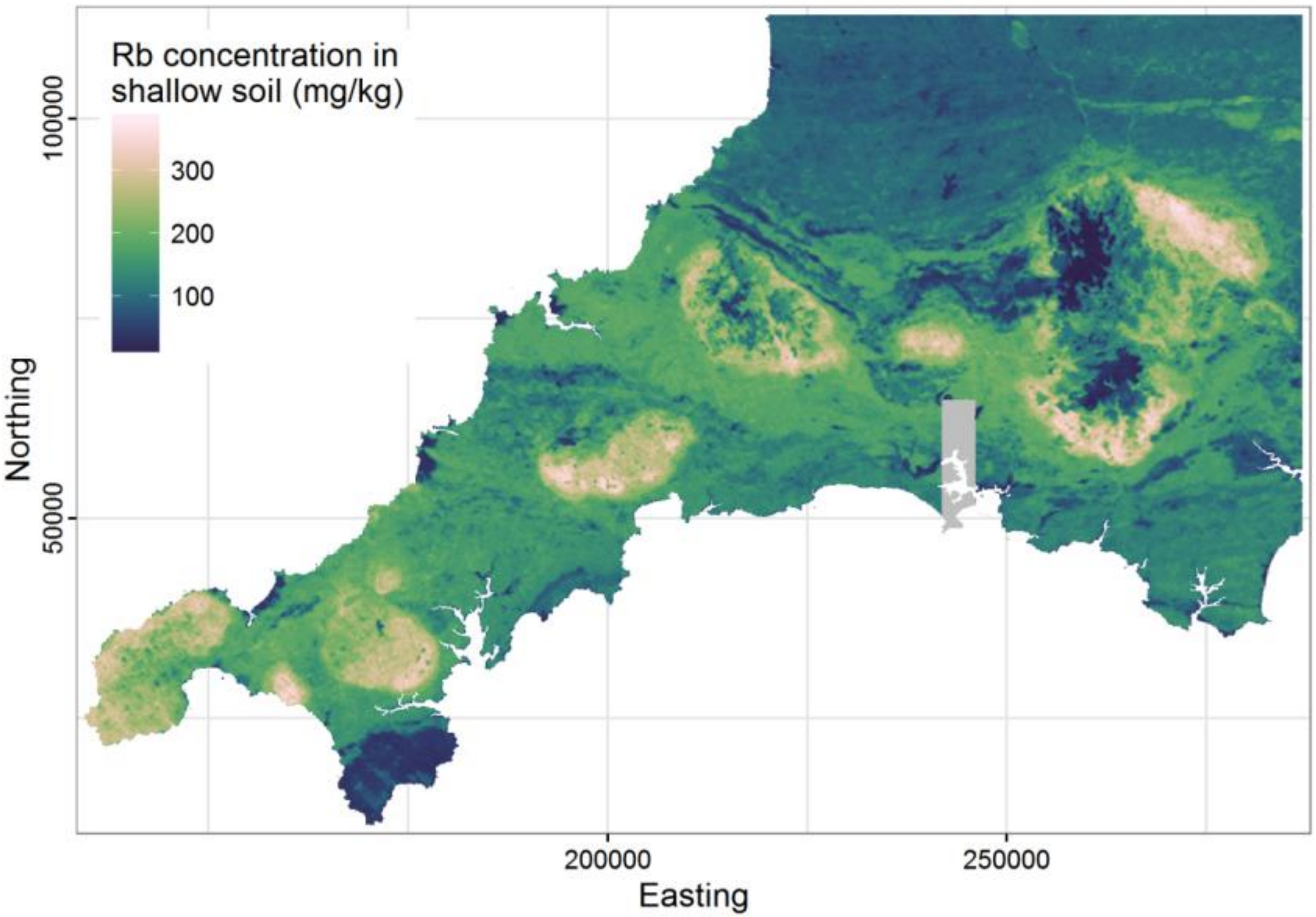


Figure 8.2. The quantile regression forest predicted concentration map for Rb in shallow soils. Created using the method of Kirkwood *et al*. (2016) by Jane Evans (*pers.com.*),

Table 8.2. All the plant samples currently known to be directly rooted in bedrock including sample code, $^{87}Sr/^{86}Sr$, the main bedrock lithology and its most common biosphere $^{87}Sr/^{86}Sr$ values and approximate difference between plants rooted in bedrock and these other biosphere values.

Sample	**Location**	**$^{87}Sr/^{86}Sr$**	**Bedrock lithology**	**Other biosphere $^{87}Sr/^{86}Sr$ on same lithology**	**$\Delta^{87}Sr/^{86}Sr$ (approximately)**
CHW 06	Charnwood Forest, England	0.71110	Precambrian Volcaniclastic sedimentry rocks.	0.71056 ±0.00024 (n=8, 2SD: (chapter 4, section 4.1.5)	0.00054
CHW 13	Charnwood Forest, England	0.71118	Precambrian Volcaniclastic sedimentry rocks.	0.71056 ±0.00024 (n=8, 2SD: chapter 4, section 4.1.5)	0.00062
LD L8	Lake District, England	0.71471	Ordovician Granitic rocks (Eskdale Pluton)	0.71053 (LD L9) and 0.71298 (ESK L1: chapter 4, section 4.7.4)	0.00173
SCOT L24	*Cairngorms National Park, Scotland*	*0.71418*	*Precambrian Quartzite*	*0.71388 ±0.00272 (n=8, 2SD: chapter 8, section 8.1.3)*	*0.00030*
FOD L3	Forest of Dean, England	0.71580	Carboniferous Coal Measures	0.71166 (FOD L4) and 0.71237 (FOD L9: chapter 7, section 7.5.2)	0.00343

Sample	Location	$^{87}Sr/^{86}Sr$	Bedrock lithology	Other biosphere $^{87}Sr/^{86}Sr$ on same lithology	$\Delta^{87}Sr/^{86}Sr$ (approximately)
JMPD_08 (NIGL, unpublished)	Peak District, England	0.71514	Carboniferous Millstone Grit	0.7116 ±0.0006 (water, n=7, 2SD: Evans *et al.,* 2010), 0.71149 (plant, JMPD_10) and 0.70954 (plant, JMPD_11: NIGL, unpublished)	0.00354

Table 8.3. All of the archaeological humans excavated in Britain with tooth enamel $^{87}Sr/^{86}Sr$ >0.713 currently. Alphabetised by location and includes information on sample code, tooth type, Sr concentration (ppm), oxygen isotopes ($\delta^{18}O$) and age of burial site where available. The last column displays the reference for each individual. For the tooth type, L=left, R=right, p= premolar, DM2= deciduous second molar, M1= permanent first molar, M2= permanent second molar and M3= permanent third molar.

Sample Code	Tooth	Sr concentration (ppm)	$^{87}Sr/^{86}Sr$	$\delta^{18}O$‰ (VSMOW)	Age	Reference
Auldhame, Scotland						
AULD-SK-158	M2	92	0.71354	17.3	Medieval	Crone & Hindmarch (2016)
Blackfriars, Gloucester, England						
341	pM1R	59	0.71423	17.9	Medieval	Montgomery (2002, p.154-160, 194, 197)
	pM1L	56	0.71429	17.5		
Boscombe and Amesbury, England						
BDLC 53535 25010	pM2	40	0.71352	17.5	Bronze Age	Fitzpatrick (2011)
6 (Boscombe)	pM2	49	0.71344	17.5	Bronze Age	Fitzpatrick (2011)
7 (Boscombe)	pM2	77	0.71309	16.9	Bronze Age	Fitzpatrick (2011

Sample Code	Tooth	Sr concentration (ppm)	$^{87}Sr/^{86}Sr$	$\delta^{18}O$‰ (VSMOW)	Age	Reference
Catterick, England						
CBF-277-M3	M3	114	0.71368	17.3	Roman	Chenery *et al.* (2011)
CBF-679-M2	M2	106	0.71367	17.7	Roman	Chenery *et al.* (2011)
Dore Abbey, Herefordshire, England						
AA-114-32	M2	72	0.71327	17.6	Medieval	Evans *et al.* (2012)
Driffield/York, England						
DRIF-15	M3	73	0.71420	18.9	Roman	Montgomery *et al.* (2011)
Ferry Fryston, West Yorkshire, England						
? (Chariot Burial)			~0.71570	~17.3	Iron Age (Chariot Burial)	Jay *et al.* (2007)
?			~0.71650	~17.1	Middle Iron Age	Jay *et al.* (2007)
?			~0.71620	~16.9	Middle Iron Age	Jay *et al.* (2007)

Sample Code	Tooth	Sr concentration (ppm)	$^{87}Sr/^{86}Sr$	$\delta^{18}O$‰ (VSMOW)	Age	Reference
?			~'0.71540	~17.8	Middle Iron Age	Jay *et al.* (2007)
?			~0.71480	~17.3	Middle Iron Age	Jay *et al.* (2007)
?			~0.71440	~16.9	Middle Iron Age	Jay *et al.* (2007)
Fin Cop, Peak District, England						
SK1			0.71550	16.3	Iron Age	Waddington *et al.* (in press)
Galson, Outer Hebrides, Scotland						
Gals-93	pM1	71	0.71303	16.1	Iron Age	Montgomery (2002, p.311-312) and Montgomery *et al.* (2003)
Gloucester, England						
GLR1561	M3	67	0.71344	18.7	Roman	Evans *et al.* (2012)
Hereford, England						
HFRD-869	M2	42	0.71401		Medieval	Evans *et al.* (2012)

Sample Code	Tooth	Sr concentration (ppm)	$^{87}Sr/^{86}Sr$	$\delta^{18}O$‰ (VSMOW)	Age	Reference
HFRD-3850	M2	66	0.71329	17.8	Medieval	Evans *et al.* (2012)
HFRD-2656	M2	87	0.71326		Medieval	Evans *et al.* (2012)
HFRD-911	M2	60	0.71302	17.9	Medieval	Evans *et al.* (2012)
Northern Scotland (unspecified)						
? (BBP)		~80	~0.71560		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~100	~0.7140		Bronze age	Parker Pearson *et al.* (2016)
? (BBP)		~140	~0.71400		Bronze age	Parker Pearson *et al.* (2016)
? (BBP)		~160	~0.71400		Bronze age	Parker Pearson *et al.* (2016)
? (BBP)		~90	~0.71360		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~50	~0.71350		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~85	~0.71330		Bronze Age	Parker Pearson *et al.* (2016)

Sample Code	Tooth	Sr concentration (ppm)	$^{87}Sr/^{86}Sr$	$\delta^{18}O$‰ (VSMOW)	Age	Reference
Parliament House, Edinburgh, Scotland						
PH SK 71	M2	77	0.71646	17.4	Medieval	Evans *et al.* (2012)
Peak District, England						
? (BBP)		~40	~0.71900		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~40	~0.71840		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~150	~0.71680		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~75	~0.71590		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~30	~0.71560		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~50	~0.71520		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~35	~0.71500		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~25	~0.71470		Bronze Age	Parker Pearson *et al.* (2016)

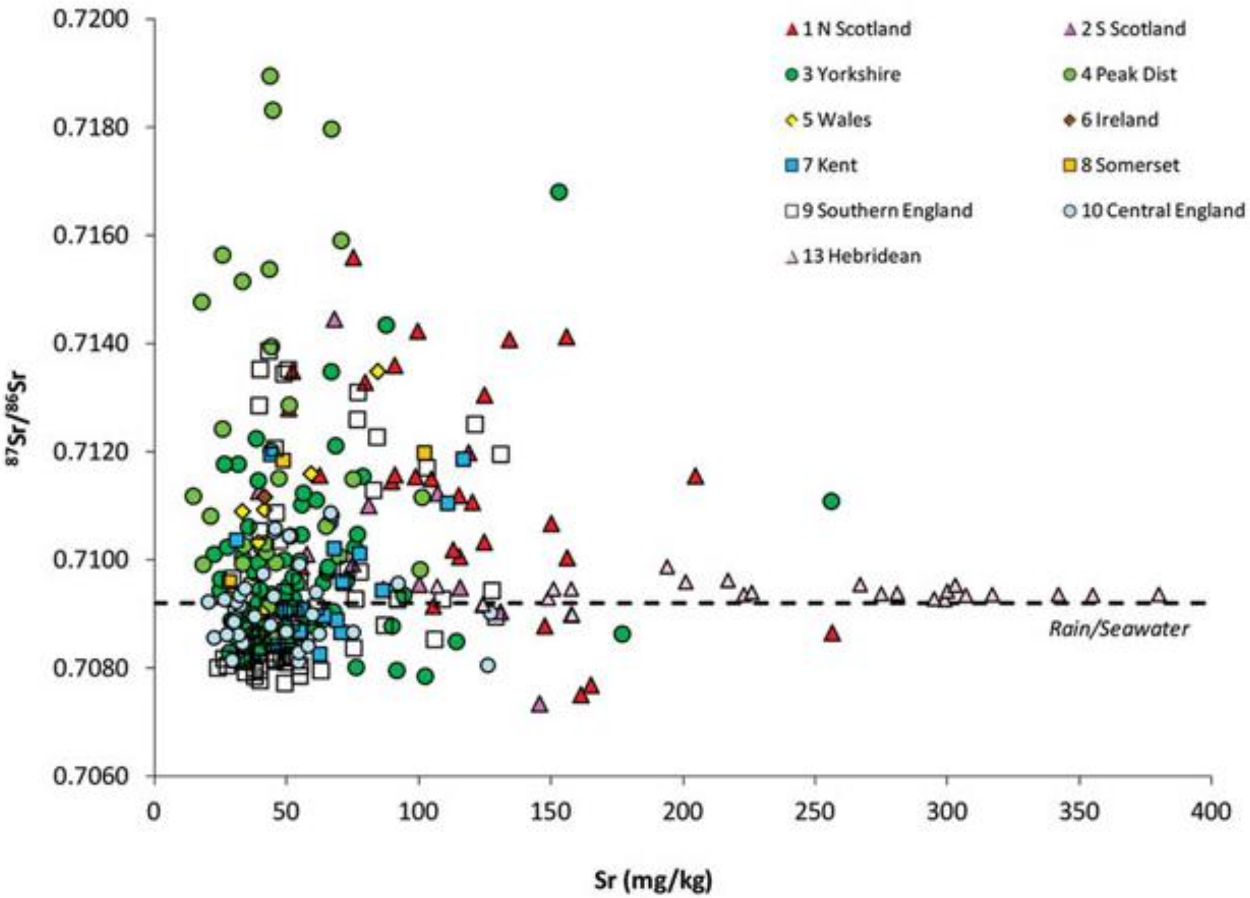
Sample Code	Tooth	Sr concentration (ppm)	$^{87}Sr/^{86}Sr$	$\delta^{18}O$‰ (VSMOW)	Age	Reference
? (BBP)		~45	~0.71390		Bronze age	Parker Pearson *et al.* (2016)
Penywyrlod, Talgarth, south-east Wales						
74.23H/9.2.3/P23	LM2	78	0.71702	17.7	Neolithic	Neil *et al.* (2017)
	LM3	62	0.71653	17		
74.23H/9.18/P20	LDM2	53	0.71583	19.4	Neolithic	Neil *et al.* (2017)
74.23H/9.7/P27	LM3	86	0.71508	18.4	Neolithic	Neil *et al.* (2017)
74.23H/9.23/P22	LM2	64	0.71501	17.5	Neolithic	Neil *et al.* (2017)
	LM3	43	0.71390	17.7		
74.23H/9.5.1/P24	LM2	89	0.71473	17.9	Neolithic	Neil *et al.* (2017)
	LM3	42	0.71335	17.8		
74.23H/9.16/P27	RM3	65	0.71472	17.2	Neolithic	Neil *et al.* (2017)

Sample Code	Tooth	Sr concentration (ppm)	$^{87}Sr/^{86}Sr$	$\delta^{18}O$‰ (VSMOW)	Age	Reference
74.23H/9.23/P21	LM2	58	0.71459	18.4	Neolithic	Neil *et al.* (2017)
	LM3	41	0.71480	18.2		
74.23H/9.7/P26	LM2	41	0.71441	17.9	Neolithic	Neil *et al.* (2017)
74.23H/9.5.19/P27	RM3	34	0.71417	17.4	Neolithic	Neil *et al.* (2017)
74.23H/9.5.11/P23	LM2	52	0.71406	17.1	Neolithic	Neil *et al.* (2017)
74.23H/9.7/P25	LDM2	97	0.71323	18.7	Neolithic	Neil *et al.* (2017)
Southern Scotland (unspecified)						
? (BBP)		~70	~0.71440		Bronze Age	Parker Pearson *et al.* (2016)
Southwest England (unspecified)						
? (BBP)		~45	~0.71380		Bronze age	Parker Pearson *et al.* (2016)
? (BBP)		~50	~0.71350		Bronze Age	Parker Pearson *et al.* (2016)

Sample Code	Tooth	Sr concentration (ppm)	$^{87}Sr/^{86}Sr$	$\delta^{18}O$‰ (VSMOW)	Age	Reference
? (BBP)		~40	~0.71350		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~50	~0.71440		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~80	~0.71320		Bronze Age	Parker Pearson *et al.* (2016)
Toremore, Arran, Scotland						
ET54	M1	68	0.71445	18.0	Bronze Age	Montgomery *et al.* (2007)
Ty Isaf, south-east Wales						
SUERC-57784	LM2	79	0.71524	16.5	Neolithic	Neil *et al.* (2017)
SUERC-57786	LM2	68	0.71436	17.9	Neolithic	Neil *et al.* (2017)
	LM3	76	0.71330	17.4		
SUERC-57789	LDM1	59	0.71409	18.4	Bronze Age	Neil *et al.* (2017)
	LDM2	64	0.71458	18.4		Neil *et al.* (2017)

Sample Code	Tooth	Sr concentration (ppm)	$^{87}Sr/^{86}Sr$	$\delta^{18}O$‰ (VSMOW)	Age	Reference
SUERC-57787 (GU36255)	LM3	102	0.71372	17.8	Neolithic	Neil *et al.* (2017)
SUERC-57785	LM3	76	0.71351	17.9	Neolithic	Neil *et al.* (2017)
SUERC-57794	LM2	78	0.71328	17.6	Neolithic	Neil *et al.* (2017)
SUERC-57796 (GU36261)	LM2	71	0.71300	17.4	Neolithic	Neil *et al.* (2017)
Wales (unspecified)						
? (BBP)		~85	~0.71350		Bronze Age	Parker Pearson *et al.* (2016)
Weymouth, England						
WEY08 SK3711	M2	95	0.71377	13.7	Medieval	Chenery *et al.* (2014))
WEY08 SK3707	M2	82	0.71306	15.1	Medieval	Chenery *et al.* (2014)
York, England						
TDC710	pM2	103	0.71355	19.7	Roman	Leach *et al.* (2009)

Sample Code	Tooth	Sr concentration (ppm)	$^{87}Sr/^{86}Sr$	$\delta^{18}O$‰ (VSMOW)	Age	Reference
TDC411	pM2	51	0.71312	17.6	Roman	Leach *et al.* (2009)
TDCR38	M2	103	0.71308	17.4	Roman	Leach *et al.* (2009)
Yorkshire, England						
? (BBP)		~70	~0.71790		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~90	~0.71430		Bronze Age	Parker Pearson *et al.* (2016)
? (BBP)		~70	~0.71350		Bronze Age	Parker Pearson *et al.* (2016)



0.7200
0.7180
0.7160
0.7140
0.7120
0.7100
0.7080
0.7060
$^{87}Sr/^{86}Sr$
0
50
100
150
200
250
300
350
400
Sr (mg/kg)
1 N Scotland
2 S Scotland
3 Yorkshire
4 Peak Dist
5 Wales
6 Ireland
7 Kent
8 Somerset
9 Southern England
10 Central England
13 Hebridean
Rain/Seawater

Location code		Median	<0.7080	<0.7092	<0.7100	<0.7110	<0.7120	<0.7130	<0.7140	<0.7150	>0.7150	Total
1 + 11	**Northern Scotland**	0.7114	2	5	1	5	8	2	4	3	1	**31**
2 + 12	**Southern Scotland**	0.7096	1	3	5	2	3	0	0	1	0	**15**
3	**Yorkshire**	0.7094	2	31	22	9	8	3	1	1	1	**78**
4	**Peak District**	0.7108	0	4	5	7	4	2	1	1	7	**31**
5	**Wales**	0.7109	0	1	0	3	1	0	1	0	0	**6**
6	**Ireland**	n/a					1					**1**
7	**Kent**	0.7091	0	9	2	3	3					**17**
8	**Somerset**	n/a			1		2					**3**
9	**Southwest England**	0.7087	10	41	11	4	2	6	5	0	0	**79**
10	**Central England**	0.7090		18	10	5						**33**
13	**Hebridean**	0.7094			21							**21**
Totals			**15**	**112**	**78**	**38**	**32**	**13**	**12**	**6**	**9**	**315**
% Total			**4.8%**	**35.5%**	**24.8%**	**12.1%**	**10.2%**	**4.1%**	**3.8%**	**1.9%**	**2.8%**	**100%**

Figure 8.3. The graph (on previous page) is Figure 6b from Parker Pearson *et al.* (2016, p.630) and displays all the enamel strontium data for Britain from the Beaker People Project (n = 264), grouped by region. The table (on this page) is the summary of all the enamel $^{87}Sr/^{86}Sr$ data for Britain from the Beaker People Project from Montgomery *et al*. (forthcoming).

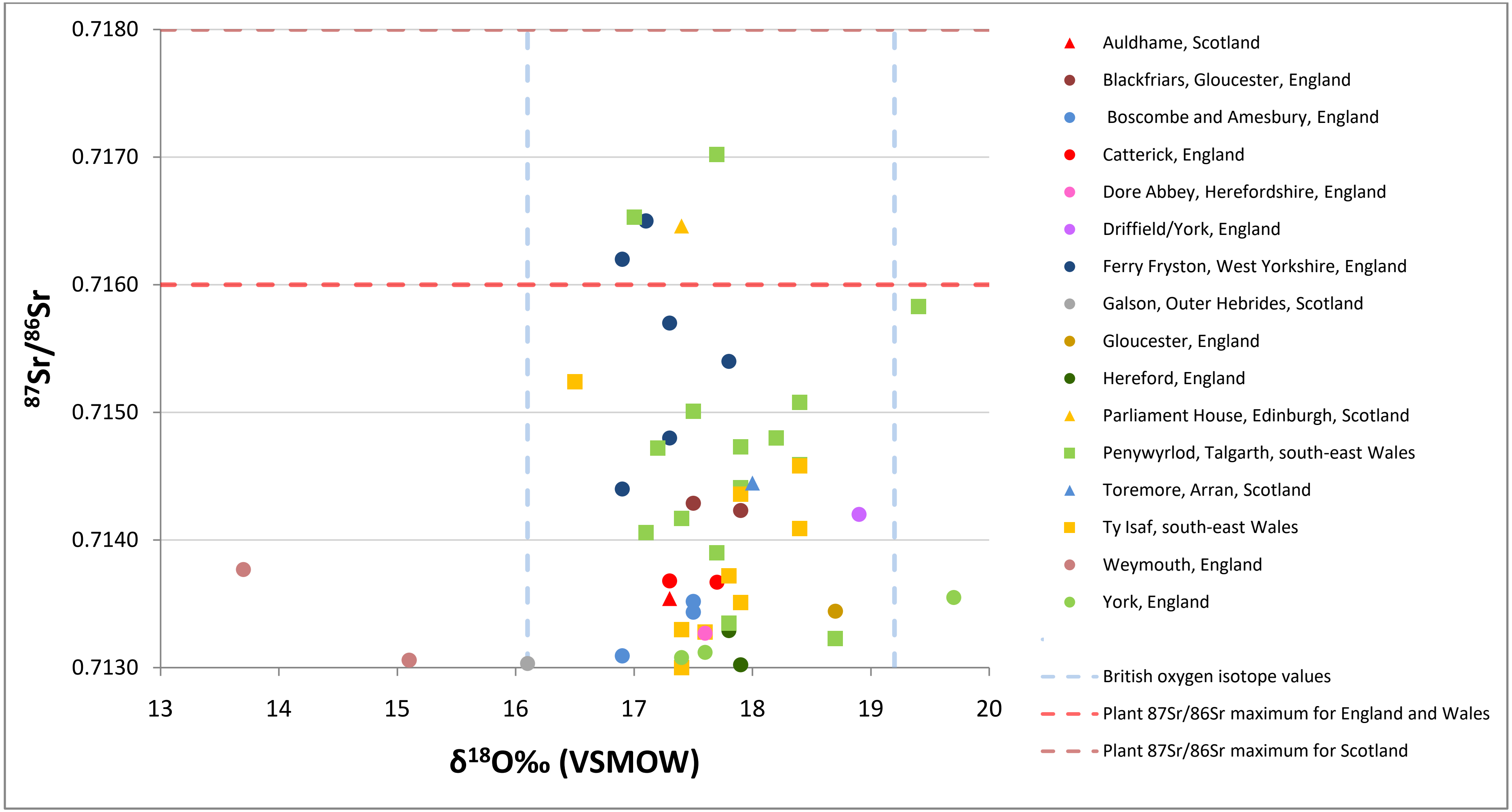


Figure 8.4. All of the archaeological humans buried in Britain with enamel $^{87}Sr/^{86}Sr$ >0.713, compared to their $\delta^{18}O$‰ (VSMOW) if available. This data can also be viewed, along with reference for each individual, in Table 8.3.

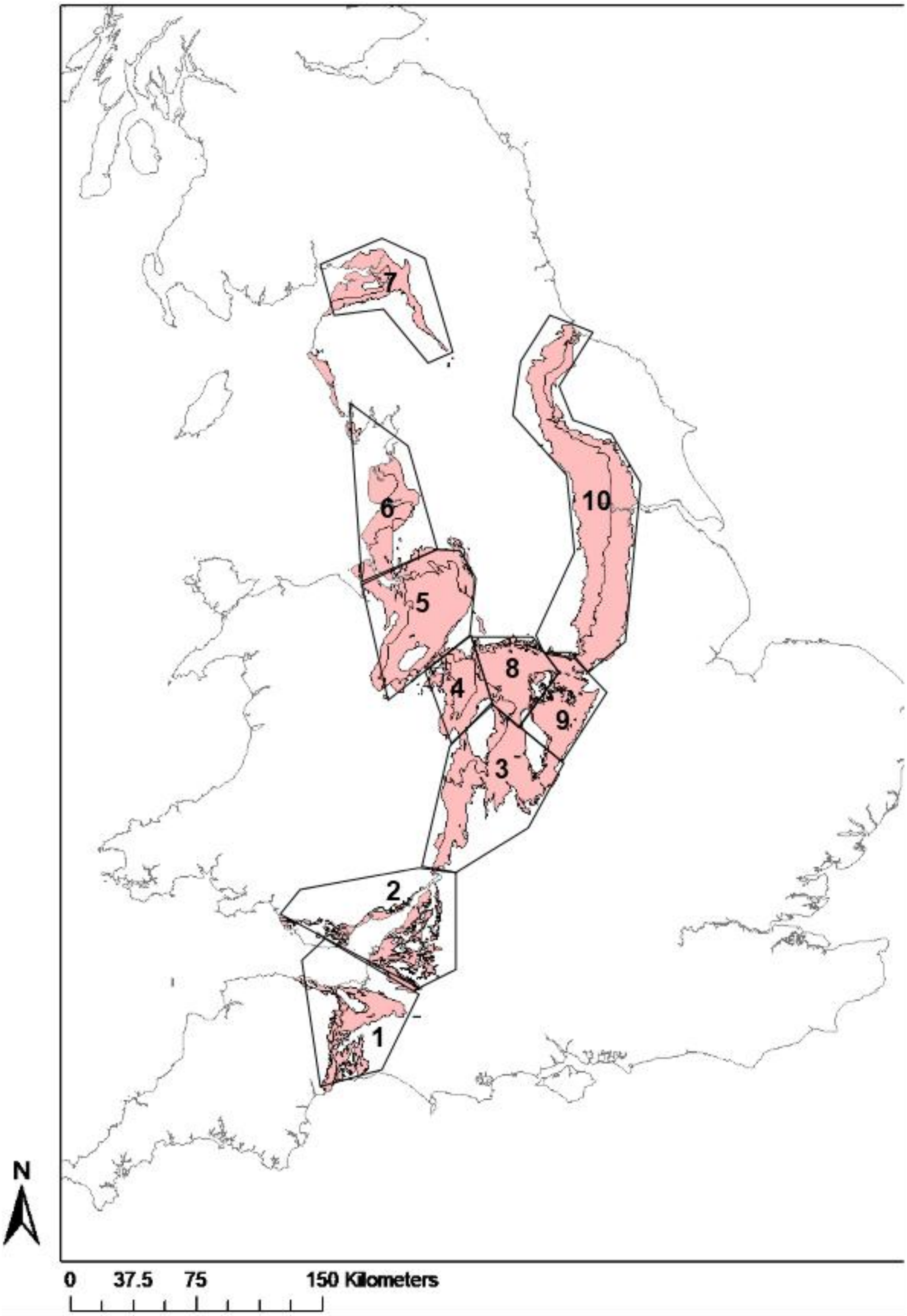


Figure 8.5. The Triassic Basins in Britain using GIS data from the 1:625000 Bedrock Geology map(BGS, DiGMapGB, 2007): 1. Wessex Basin; 2.Bristol/South Wales Basin; 3.Worcester/Knowle Basin; 4.Stafford Basin; 5.Cheshire Basin; 6.West Lancashire; 7.Carlisle Basin; 8.Needwood Basin; 9.Hinckley Basin; 10.East Midlands Shelf (adapted from Figure 1 in Howard *et al.,* 2008, p.23).

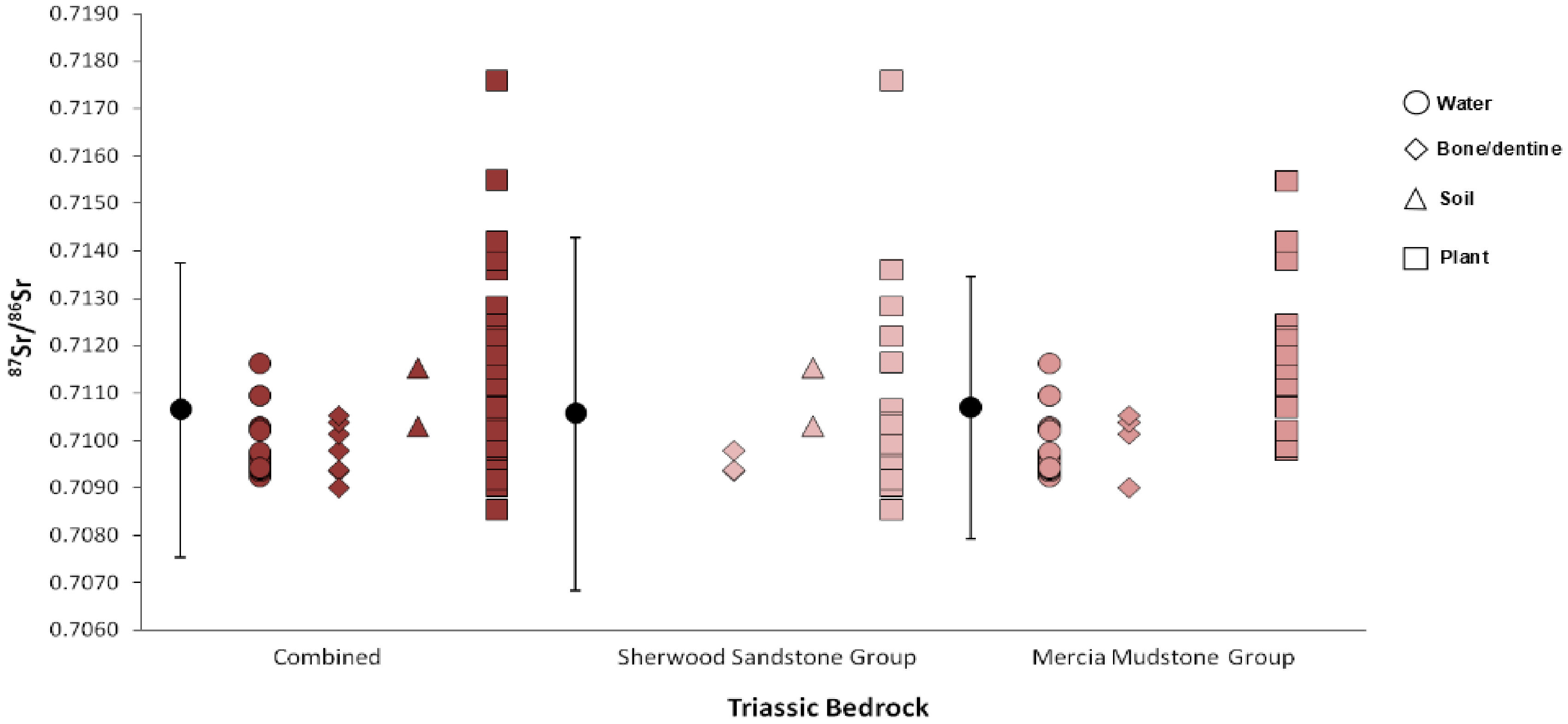


Figure 8.6. The biosphere $^{87}Sr/^{86}Sr$ data overlying the Triassic bedrock in Britain as a whole and split into the Sherwood Sandstone Group and the Mercia Mudstone Group. The black circle and lines represent the mean and standard deviation (2SD) for the all the biosphere $^{87}Sr/^{86}Sr$ data on the Triassic bedrock combined and the two lithostratigraphical groups. Biosphere $^{87}Sr/^{86}Sr$ data comes from Spiro *et al.,* (2001); Montgomery *et al.,* (2006); Trickett, (2007); Leach *et al.,* (2009); Montgomery *et al.,* (2009); Chenery *et al.,* (2010); Evans *et al.,* (2010); Chenery *et al.,* (2011); Evans, *pers.com*.; NIGL, unpublished; chapter 4, section 4.1, 4.2.4.3; chapter 6.

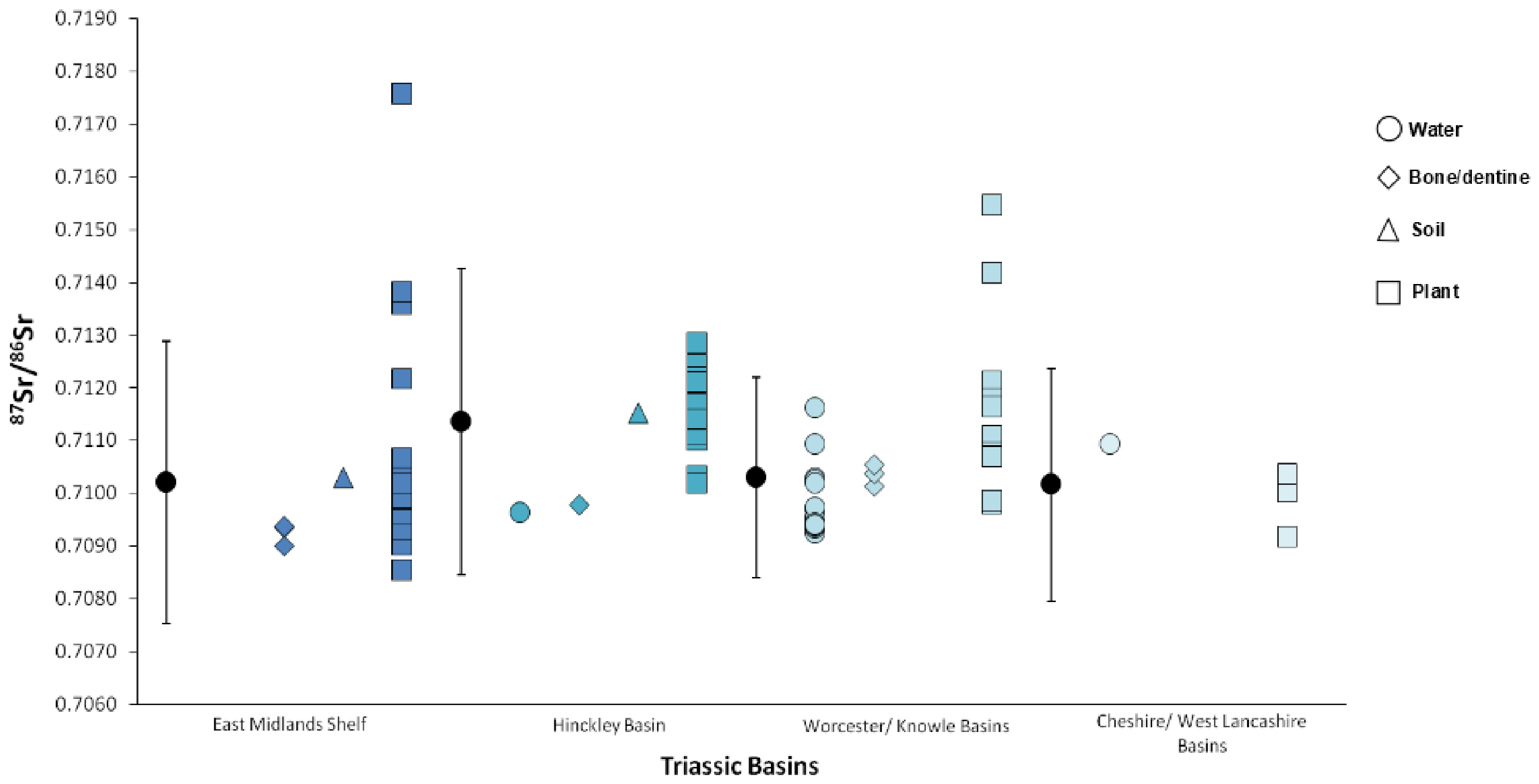


Figure 8.7. The Triassic biosphere $^{87}Sr/^{86}Sr$ data from the Cheshire/West Lancashire Basins, East Midlands Shelf, Hinckley Basin and Worcester/Knowle Basins. For the locations of Triassic Basins in Britain see Figure 8.5. The black circle and lines represent the mean and standard deviation (2SD) of each basin. Biosphere $^{87}Sr/^{86}Sr$ data comes from Spiro *et al.,* (2001); Montgomery *et al.,* (2006); Trickett, (2007); Leach *et al.,* (2009); Montgomery *et al.,* (2009); Chenery *et al.,* (2010); Evans *et al.,* (2010); Chenery *et al.,* (2011); Evans, *pers.com*.; NIGL, unpublished; chapter 4, section 4.1, 4.2.4.3; chapter 6.

9. Conclusions

High $^{87}Sr/^{86}Sr$ >0.714 only represent 10% of all known British Sr-isotope biosphere data. These values occupy an area equivalent to 2.8% of Britain, making them spatially rare in Britain (chapter 8, section 8.1) and can also be considered agriculturally marginal for archaeological populations.

In Scotland, the areas known to produce radiogenic biosphere values >0.716 include: the Silurian Cairngorm suite and the biosphere aureole to the north in the Cairngorms National Park (chapter 8, section 8.1.1.1, section 8.1.2.); around Lairg, Sutherland, based on Precambrian psammites of the Highland terrane (Evans *et al.,* 2010); the biosphere aureole around the Tertiary granites on the Isle of Skye (Evans *et al.,* 2009). These same areas in Scotland can also produce biosphere $^{87}Sr/^{86}Sr$ >0.714, with the addition of any areas overlying the Precambrian Dalradian quartzite formations (chapter 8, section 8.1.3). Scotland has a maximum plant $^{87}Sr/^{86}Sr$ = 0.718, while water values are expected to have a maximum value ~0.720 (chapter 8. Section 8.1.1.1). In England and Wales, the areas known to produce radiogenic biosphere values up to 0.716 include: the Precambrian Malvern Complex of the Malvern Hills (chapter 4, section 4.2); the Silurian Ludlow sedimentary rocks along the Welsh Border, from the village of Boughrood (Powys, Wales) to the outskirts of the Precambrian Longmydnian bedrock near Church Stretton (section 8.1.1.2); the Lower Palaeozoic mudstones and shales in central Wales. The last area, on the Lower Palaeozoic mudstones and shales, is based on ground and stream water $^{87}Sr/^{86}Sr$ (Shand *et al.,* 2007) and it is not known if plant $^{87}Sr/^{86}Sr$ from the same area will produce the same high $^{87}Sr/^{86}Sr$ values as seen by the water samples. England and Wales have a maximum plant $^{87}Sr/^{86}Sr$ = 0.716, while the maximum water $^{87}Sr/^{86}Sr$ = 0.715 (chapter 8, section 8.1.1.2). Any archaeological humans, or animals, excavated in Britain with enamel $^{87}Sr/^{86}Sr$ >0.714, who are not considered local to their burial environment, can only have originated from the areas above in Britain, otherwise they can be assumed to have originated from outside of Britain. Whether these areas also coincide with other archaeological or isotopic evidence, such as $\delta^{18}O$ values, to suggest migration from such places needs to also be considered in interpretations.

The preliminary study into plant $^{87}Sr/^{86}Sr$ collected from ancient woodlands vs. agricultural land has indicated that woodlands have elevated values by approximately

+0.002 compared to agricultural land (chapter 6). The plants collected from agricultural land were not taken directly from any arable fields, only the tree verges and open land that surrounds them, but are assumed to still be influenced by agricultural practices. For example, the Sherwood Forest Nature Reserve in Nottinghamshire, England, has recorded plant $^{87}Sr/^{86}Sr$ of 0.71218 (SF L4), 0.71358 (SF L1) and 0.71757 (SF L3), which are elevated in value compared to plant $^{87}Sr/^{86}Sr$ on agricultural land at 0.7098 ±0.00082 (n=4, 2SD) (chapter 6, section 6.4.1). However, these results are speculative and further work is needed to confirm if this woodland trend is replicated elsewhere in Britain and to define the changes in plant $^{87}Sr/^{86}Sr$ in biospheres hosted by different bedrock lithologies. If such woodland trends continue, more biospheres with high $^{87}Sr/^{86}Sr$ >0.714 may be characterized in Britain, but they are not expected to surpass the current maximum values stated above for Scotland, England and Wales.

Biosphere $^{87}Sr/^{86}Sr$ >0.720 in Britain, as reported by Evans *et al.* (2010), have not been reproducible in this thesis. Such biosphere values >0.720 regularly occur on the Precambrian granitic regions of Scandinavia (Åberg & Wickman, 1987; Åberg *et al.,* 1998; Sjögren *et al.,* 2009; Voerkelius *et al.,* 2010; Frei & Frei, 2011; 2013; Sjögren & Price, 2013; Price *et al.,* 2017). In Scandinavia, the Precambrian granites and strongly metamorphic gneisses formed in plutonic intrusions of the Baltic Shield and can dominant the bedrock geology for 100s of kilometres (Figure 2.5 in chapter 2). Precipitation in inland Scandinavia can have high $^{87}Sr/^{86}Sr$ >0.714 (Åberg *et al.,* 1989: Andersson *et al.,* 1990), because of the incorporation of terrestrial dust, which potentially originates from the Precambrian granites and gneisses. Also in their investigation of soil profiles in Sweden, Åberg *et al.* (1990) showed that within the first 20cm depth of the soil, the loss of Ca minerals through weathering and the enrichment in more resistant K-minerals (rich in radiogenic ^{87}Sr) has resulted in higher $^{87}Sr/^{86}Sr$ values compared to the deeper soils. This has all resulted in the Sr-isotope biospheres in Scandinavia being able to produce $^{87}Sr/^{86}Sr$ >0.720.

In comparison, Britain's bedrock geology is incredibly varied, from the Precambrian igneous and metamorphic rocks found mainly in northern Scotland, through to the Cretaceous Chalks and Tertiary sedimentary rocks in south-east England. Although large igneous intrusions can be found in Britain, such as the Siluro-Devonian 'Caledonian granite' supersuite in Scotland which altogether cover approximately 2400km^2, they do not compare in size to the plutonic intrusions of the Baltic Shield in Scandinavia. The bedrock geology of Britain has resulted in a large range of biosphere $^{87}Sr/^{86}Sr$ values being available. If considering plant $^{87}Sr/^{86}Sr$, as plants are the dominant dietary input of Sr into humans (Burton & Wright, 1995; Montgomery, 2010), Britain has a minimum value at 0.7075 ±0.0011 (n=7, 1SD) on the Tertiary bedrock in Scotland (Evans *et al.,* 2010) and a maximum value at 0.7174 ±0.0049 (n=7, 2SD) which are potentially on the thermal aureole of the Cairngorm suite in Scotland (chapter 5, section 5.4.1 and 5.5). However, the main influencer to why biosphere $^{87}Sr/^{86}Sr$ >0.720 are so rare in Britain, is rainwater. In Britain, the majority of the precipitation, e.g. rainwater, does not substantially deviate from the marine value of 0.7092 (Veizer, 1989, p.142), only showing some degree of geographic variation by ±0.0005 (n=15, 2SD) at elevated, inland sites and regionally by the influence of any potential radiogenic bedrock outcrops (Warham, 2011, p.150-163). The western coast of Britain can averagely experience >1000mm of rainfall annually, with some inland elevated sites reaching over 3000mm of rainfall annually (Met Office 1981-2010 Rainfall Amount Annual Average Map). Such high rainfall causes high saturation of the soil, resulting in the $^{87}Sr/^{86}Sr$ from precipitation dominating the local Sr-isotope biosphere and this can be seen through the $^{87}Sr/^{86}Sr$ of soils, plants and animals (Evans *et al.,* 2010; Montgomery *et al*., 2014). If precipitation in Britain had similar $^{87}Sr/^{86}Sr$ values as seen in Scandinavia, at >0.714, perhaps some of the areas that already produce biosphere $^{87}Sr/^{86}Sr$ >0.714 could record values >0.720, but this is not the case. Overall, biosphere $^{87}Sr/^{86}Sr$ values >0.720 are extremely rare in Britain. Therefore, based on all the known British Sr-isotope biosphere data currently, any archaeological humans or animals excavated in Britain with high enamel $^{87}Sr/^{86}Sr$>0.720 have potentially not originated from Britain.

Even the ingestion of rock or soil has been shown not to alter the skeletal $^{87}Sr/^{86}Sr$ of a human in any significant manner (e.g. by +0.001 or greater) (chapter 7). Rock grit unintentionally consumed as a result of using quern or millstones to grind grain is unlikely to equate to more than 1% of the diet (by mass and calorific intake). Although the Sr within rock grit is bioaccessible by the human digestion system, often producing values similar to the biosphere $^{87}Sr/^{86}Sr$ on the grinding stone's lithology, at the 1% level ingested grit will not result in a significant change in human $^{87}Sr/^{86}Sr$ values. Consequently, the use of querns or millstones and the regular unintentional consumption of their grit, whether of locally-derived or imported rock, will have a negligible effect on human $^{87}Sr/^{86}Sr$ data and will neither produce anomalously high skeletal $^{87}Sr/^{86}Sr$ values nor false migrants. The intentional consumption of rock, clays or soils through geophagy or pica, which is difficult to identify in the archaeological record, is also unlikely to adversely affect skeletal $^{87}Sr/^{86}Sr$. The results of this study (chapter 7) thus provide reassurance to researchers using Sr-isotope analysis to identify migrants in Britain and elsewhere, that non-local or unusually high $^{87}Sr/^{86}Sr$ values cannot be explained by the direct ingestion of rock grit, clays or soils.

The following sections in this conclusion provide a concise review into the important implications for archaeological migration and mobility studies this research has explored (section 9.1), the main findings in relation to the original research questions (section 9.2) and suggestions for further research into Sr-isotope biospheres in Britain (section 9.3).

9.1. Important implications for archaeological mobility and migration studies in Britain

There are some important points from this research that need to be reiterated. From all the current Sr-isotope biosphere data currently available for Britain, values >0.714 only occupy an area equivalent to 2.8% of Britain. This means there is currently a very limited number of places that archaeological humans and animals excavated in Britain with enamel $^{87}Sr/^{86}Sr$ >0.714 could have originated from, if they are considered to be British. The majority of these areas are also located at high elevations on granitic lithologies which often results in poor acidic soils and wet conditions that are unattractive for agriculture. For the archaeological populations relying on agricultural for sustenance, these areas are impractical for long-term survival. The only exceptions may be the biosphere aureole to the north in the Cairngorms National Park in Scotland (chapter 8, section 8.1.2.) and the Silurian Ludlow sedimentary rocks along the Welsh Border, (section 8.1.1.2), in which plant and water samples have recorded $^{87}Sr/^{86}Sr$ >0.714 at elevations more suitable for agricultural and in which modern arable farming has been recorded (Appendix 2). Overall the majority of the high Sr-isotope biospheres in Britain can be considered agriculturally marginal, but still need to be considered when interpreting human and animal enamel $^{87}Sr/^{86}Sr$ in Britain. Therefore the following statements are recommended:

1. Biosphere values >0.720 are extremely rare and not consistent in the Britain. None of the 151 plant samples analysed in this thesis have recorded $^{87}Sr/^{86}Sr$ values >0.720 and the 'hotspots' with values ~0.720 reported in Evans *et al.* (2010) have not been reproducible. Therefore it would be very reasonable to suggest that archaeological humans and animals with enamel $^{87}Sr/^{86}Sr$ >0.720 are non-British in origin. Currently biosphere values >0.720 are only found consistently on the Precambrian granitic regions of Scandinavia (Åberg & Wickman, 1987; Åberg *et al.,* 1998; Sjögren *et al.,* 2009; Voerkelius *et al.,* 2010; Frei & Frei, 2011; 2013; Sjögren & Price, 2013; Price *et al.,* 2017).
2. Archaeological humans and animals with enamel $^{87}Sr/^{86}Sr$ >0.718 are also unlikely to have originated from Britain. This is based on the plant $^{87}Sr/^{86}Sr$ data currently available in Britain, as plants are the dominant dietary input of Sr into humans (Burton & Wright, 1995; Montgomery, 2010). Scotland has a maximum plant $^{87}Sr/^{86}Sr = 0.718$ (chapter 8. Section 8.1.1.1). Although there are a handful of plant samples with $^{87}Sr/^{86}Sr$ >0.718 found in Scotland (Evans *et al.* 2010), they are not consistent and often found near to much lower biosphere $^{87}Sr/^{86}Sr$ values, which ultimately results in a lower mean $^{87}Sr/^{86}Sr$ for the area. It is not good practice to consider a location as a potential origin of a person or animal based on the value of one point-sample. Outside of the Precambrian granitic regions of Scandinavia, biosphere values >0.718 are rare in Europe but the granitic and metamorphic lithologies of the Bohemian Massif and Black Forest in Germany (Bentley & Knipper, 2005; Voerkelius *et al.,* 2010; Oelze *et al.,* 2012), the gneiss bedrock of Central Alps (Hoggewerff *et al.,* 2001) and on and around Central Massif in France (Willmes *et al,* 2014) may be worthy of consideration. Currently only two Bronze Age humans excavated in the Peak District as part of the Beaker People Project have recorded enamel $^{87}Sr/^{86}Sr$ >0.718 (Parker Pearson *et al.*, 2016; Montgomery *et al*., forthcoming), so it is can be confidently assumed that these individuals are unlikely to be British in origin.
3. Only Scotland currently produces biosphere $^{87}Sr/^{86}Sr = 0.716$- 0.718 consistently and these are only at three select locations including: the Silurian Cairngorm suite

and the biosphere aureole to the north in the Cairngorms National Park (chapter 8, section 8.1.1.1, section 8.1.2.); around Lairg, Sutherland, based on Precambrian psammites of the Highland terrane (Evans *et al.,* 2010); the biosphere aureole around the Tertiary granites on the Isle of Skye (Evans *et al.,* 2009). Archaeological humans and animals with enamel $^{87}Sr/^{86}Sr$ between 0.716 - 0.718 can only have originated from these areas if considered British. Otherwise the same European locations as suggested in previous bullet point would be acceptable suggestions of origin. There are currently six archaeological humans who have enamel $^{87}Sr/^{86}Sr$ >0.716, but <0.718, excavated from Neolithic Penwyrlod (south-east Wales: Neil *et al.*, 2017), Bronze Age Peak District and Yorkshire (Parker Pearson *et al.*, 2016; Montgomery *et al*., forthcoming), Iron Age Ferry Fryston (West Yorkshire: Jay *et al.*, 2007) and medieval Edinburgh (Evans *et al.,* 2012). It would be reasonable to suggest that the latter medieval individual may be a Scottish migrant from the Cairngorms National Park, which is approximately 160km north of Edinburgh. The biosphere $^{87}Sr/^{86}Sr$ data obtained in this thesis can also provide further support to Neil *et al.* (2017) interpretations of having a non-British Neolithic migrant at Penwyrlod (south-east Wales). However, more isotope data and archaeological evidence is needed before making similar suggestions for the remaining Bronze Age (Parker Pearson *et al.*, 2016; Montgomery *et al*., forthcoming) and Iron Age (Jay *et al.*, 2007) individuals, which is not currently available.

4. Archaeological humans and animals with enamel $^{87}Sr/^{86}Sr$ between 0.714-0.716 have several more possible areas of origin within Britain compared to those with values >0.716. The same locations in Scotland as in the above bullet point are still viable with the addition any areas overlying the Precambrian Dalradian quartzite formations (chapter 8, section 8.1.3). In England and Wales the Precambrian Malvern Complex of the Malvern Hills (chapter 4, section 4.2), the Silurian Ludlow sedimentary rocks along the Welsh Border (section 8.1.1.2) and the Lower Palaeozoic mudstones and shales in central Wales (based on ground and stream water $^{87}Sr/^{86}Sr$: Shand *et al.,* 2007) are all possible areas of origin too. More places of origin can be considered in Europe too, including the locations previously suggested with the addition of areas in Lower Normandy, Brittany and Pays de la Loire in north-western France, on the Armorican Massif of western France, (*Willmes et al.*, 2014), the Vosges Mountains of France (Bentley *et al.,* 2003;

Voerkelius *et al.*, 2010) a*nd the* Iberian Massif of Portugal and western Spain (Voerkelius *et al.,* 2010; Díaz-Zorita Bonilla, 2013, p.186-201).

5. The analysis of human and animal enamel and biosphere Sr-isotope data can only be used to state whether the individual in question is local to their burial location or not. This Sr-isotope data is best use in conjunction with other isotope data (oxygen, lead, carbon, nitrogen, etc.) and archaeological evidence and cannot be used to definitely state where someone originated from, only suggest potential possibilities.

9.2. Thesis findings in relation to the main Research Questions

1: Finding high $^{87}Sr/^{86}Sr$ biospher*es in E*ngland and Wales?

- The majority of the English study areas in this thesis have not prod*uced pl*ant $^{87}Sr/^{86}Sr$ >0.714, with the highest values being approximately 0.712. These include: Charnwood Forest (Leicestershire: chapter 4, section 4.1); Nuneaton (Warwickshire: chapter 4, section 4.3); the Wrekin (Shropshire: chapter 4, section 4.5); the Lake District (chapter 4, section 4.7).
- The Precambrian Malvern Complex, which forms the Malvern Hills, have biosphere $^{87}Sr/^{86}Sr$ = 0.7133 ±0.0031 (n=11, 2SD: Montgomery *et al.,* 2006; Chenery *et al.,* 2010; Evans, unpublished results; *pers.com*.; chapter 4, section 4.2), with the highest plant $^{87}Sr/^{86}Sr$ = 0.71622 (G-V-026: Chenery *et al.,* 2010).
- An aureole of high plant $^{87}Sr/^{86}Sr$>0.714 (CS L2, CS L3 and CS L12) and one slightly lower value at 0.71374 (CS L6), are found at lower elevations around the Precambrian Uriconian and Longmyndian in the Church Stretton study area (chapter 4, section 4.4). This aureole may be the result of the weathering and erosion of the Precambrian lithologies (chapter 4, section 4.4) or may be influenced by the thermal aureole of the Ordovician granite intrusion approximately 5-10km under the surface (chapter 8, section 8.1.2)
- The Silurian Ludlow sedimentary rocks near the market town of Kington, Herefordshire, England and the village of Boughrood, Powys, Wales, have

biosphere $^{87}Sr/^{86}Sr$ = 0.7135 ±0.0040 (n=7, 2SD) (Evans, *pers com.*: chapter 4, section 4.6), with the highest plant $^{87}Sr/^{86}Sr$ = 0.71613 (SHC L6: chapter 4, section 4.6).

- The Lower Palaeozoic shales and mudstones in the catchment of Plynlimon, central Wales have mean ground water $^{87}Sr/^{86}Sr$ = 0.7139 ±0.0030 (n=25, 2SD) and stream water $^{87}Sr/^{86}Sr$ = 0.7130 ±0.0016 (n=20, 2SD)(Shand *et al.,* 2007). Just the ground waters on the Ordovician bedrock have $^{87}Sr/^{86}Sr$ = 0.7130 ±0.0008 (n=11, 1SD: Evans *et al.,* 2010). It is not known if plant $^{87}Sr/^{86}Sr$ will produce similar values as the water samples in this area (chapter 8, section 8.1.1.2).

<u>2: Are the high biosphere $^{87}Sr/^{86}Sr$ in Scotland reproducible, particularly values >0.720?</u>

- None of the high biosphere $^{87}Sr/^{86}Sr$ >0.720 in the Cairngorms National Park, Scotland, reported by Evans *et al.* (2010) have been reproducible by the plant $^{87}Sr/^{86}Sr$ collected in this thesis (chapter 5).
- The Silurian Cairngorm suite, that form the Cairngorm mountains, have biosphere $^{87}Sr/^{86}Sr$ = 0.7155 ±0.0014 (n=8, 2SD: chapter 5).
- North of the Cairngorm mountains, around the base of the Silurian Cairngorm and Monadhliath Plutons have biosphere$^{87}Sr/^{86}Sr$ = 0.7174 ±0.0049 (n=7, 2SD: chapter 5, section 5.4.1 and 5.5). The thermal aureole of these plutons, which can result in high rubidium (Rb) concentrations (ppm) in the overlying soil, may be the reason to why there are the high biosphere $^{87}Sr/^{86}Sr$ recorded in this area (chapter 8, section 8.1.2).
- The Precambrian Dalradian quartzite formations in the Grampian terrane of Scotland have plant $^{87}Sr/^{86}Sr$ = 0.7139 ±0.0027 (n=8, 2SD: chapter 8, section 8.1.3).

<u>3: What are the maximum plant $^{87}Sr/^{86}Sr$ in Britain?</u>

- For Scotland, the maximum plant $^{87}Sr/^{86}Sr$ = 0.718 and is based on the plant sample SCOT GL3 at 0.71820, north of the Cairngorm mountains and the plant

$^{87}Sr/^{86}Sr$ = 0.7178 ±0.0022 (n=4, 2SD), on the Northern Highland terrane (Evans *et al.,* 2010).

- For England and Wales, the maximum plant $^{87}Sr/^{86}Sr$ = 0.716 and is based on the plant samples G-V-026 at 0.71622 on the Precambrian Malvern Complex, Malvern Hills (Chenery *et al.,* 2010) and SHC L6 at 0.71613 on the Silurian Ludlow sedimentary rocks, near Kington, Herefordshire (chapter 4, section 4.6).
- For Scotland, the maximum water $^{87}Sr/^{86}Sr$ is expected to be ~0.720, based on water samples reported by Bacon & Bain (1994) and by Evans *et al.,* (2010) (chapter 8, section 8.1.1.1.).
- For England and Wales, the maximum water $^{87}Sr/^{86}Sr$ = 0.715 and is based on the ground water sample VB 1 at 0.71521 on the Lower Palaeozoic shales and mudstones in the catchment of Plynlimon, central Wales (Shand *et al.,* 2007) (chapter 8, section 8.1.1.2).

<u>4: Can any other environmental reasons lead to high $^{87}Sr/^{86}Sr$ in the biospheres of Britain?</u>

- The woodland effect (chapter 2, section 2.4.3) has the potential to alter the Sr-isotope biosphere of a woodland towards higher $^{87}Sr/^{86}Sr$ values. A preliminary study comparing the plant $^{87}Sr/^{86}Sr$ of ancient woodlands vs. agricultural land on the Triassic bedrock of central England have shown that woodland plant $^{87}Sr/^{86}Sr$ can be higher in value by approximately +0.002 compared to agricultural land (chapter 6). Further work is needed to confirm if this trend is replicated elsewhere in Britain and to define the changes in plant $^{87}Sr/^{86}Sr$ in biospheres hosted by different bedrock lithologies. If this trend continues, it could have major implications to how biosphere and archaeological human $^{87}Sr/^{86}Sr$ data are interpreted in migration and mobility studies (chapter 8, section 8.2.1).
- The plant samples recorded as directly rooted in exposed rock in this thesis have $^{87}Sr/^{86}Sr$ that are elevated in value by approximately +0.0017 to +0.0030 compared to other plant samples, not rooted in the exposed rock, overlying the same bedrock lithology. This observation highlights a previously unrecognised way in which high plant $^{87}Sr/^{86}Sr$ >0.714 could be obtained, but it is expected that such

plants will not realistically be ingested in enough quantity to alter human or animal $^{87}Sr/^{86}Sr$ (chapter 8, section 8.1.4).

<u>5: Is the $^{87}Sr/^{86}Sr$ of rock grit ingested by humans bioaccessible and therefore can alter human $^{87}S/^{86}Sr$?</u>

- Through the use of the Unified Bioaccessibility Method (UBM: Hamilton *et al.,* 2015), Sr in rock grit, whether accidently ingested via the use of grinding stones or deliberately through pica or geophagy, is rendered bioaccessible by the strong acids of the human gut (chapter 7, section 7.5.1).
- The bioaccessible component of rock grit, ingested through the use of a quern or millstone to grind grain, usually has $^{87}Sr/^{86}Sr$ values similar to the observed biosphere $^{87}Sr/^{86}Sr$ on the grinding stone's lithology(chapter 7, section 7.6.1).
- Theoretically, the rock grit unintentionally consumed as a result of using quern or millstones to grind grain is unlikely to equate to more than 1% of the diet (by mass and calorific intake). At the 1% level, regardless of the grinding stone's lithology or the local Sr-isotope biosphere, ingested grit will not result in a significant change (e.g. ±0.001 or greater) in human $^{87}Sr/^{86}Sr$ values (chapter 7, section 7.6.2).
- Even the intentional consumption of rock, clays or soils through geophagy or pica, which is difficult to identify in the archaeological record, is unlikely to adversely affect human skeletal $^{87}Sr/^{86}Sr$. It is theoretically estimated that the consumption of chalk (~0.708), on a millstone grit Sr-isotope biosphere(~0.711), would still need to comprise >13% of the diet (by mass and calorific intake) on a regular basis to significantly shift human skeletal $^{87}Sr/^{86}Sr$ by -0.001 (chapter 7, section 7.6.2).

9.3. Further research into Sr-isotope biospheres in Britain

Further research is needed into the woodland effect (chapter 2, section 2.4.3) and plant $^{87}Sr/^{86}Sr$ in ancient woodlands in Britain. The ancient woodlands on the Triassic bedrock of central England and the Silurian Ludlow sedimentary rocks near the Welsh border have plant $^{87}Sr/^{86}Sr$ values that are elevated by approximately +0.002 compared to plant $^{87}Sr/^{86}Sr$ collected from agricultural land (chapter 6). This woodland trend is still speculative and needs to be confirmed by broader sampling of the preliminary study of Sherwood Forest (Nottinghamshire). The addition of Sr-isotope analysis of any local archaeological fauna samples (wild and domestic), if available, would also be beneficial for comparison. Further sampling from different ancient woodlands across Britain could define the changes in plant $^{87}Sr/^{86}Sr$ in biospheres hosted by different bedrock lithologies. The ancient woodlands of New Forest (south England) on the Eocene sedimentary bedrock, Inglewood Forest (Cumbria) on the Permian sandstone and conglomerate bedrock and Kielder Forest (Northumberland) on the Carboniferous sedimentary bedrock may be good additions and comparisons to Sherwood Forest.

The woodland effect could have major implications to how biosphere and human $^{87}Sr/^{86}Sr$ data are interpreted in archaeological migration and mobility studies. If the woodlands in Britain can alter their own biosphere through the woodland effect, they will need to be seen as a separate domain during Sr-isotope biosphere mapping. Also, any archaeological studies using Sr-isotope analysis on humans and animals pre-dating the Roman period will have to carefully consider the woodland effect when using modern biosphere proxy data to define what $^{87}Sr/^{86}Sr$ values are considered location to their burial site or sites (chapter 8, section 8.2.1). It is expected that woodlands will affect the plant $^{87}Sr/^{86}Sr$ greatest on lithologies where the carbonate minerals can be leached out over time, such as mud- and siltstones, probably resulting in a difference of +0.002 or greater between woodland and agricultural plant $^{87}Sr/^{86}Sr$. Limestone or chalk bedrock, consisting purely of carbonate minerals, will potentially show no difference between woodland and agricultural land plant $^{87}Sr/^{86}Sr$ because of their homogenous nature. It is currently hard to predict what change, if any, will occur between woodland and agricultural land plant $^{87}Sr/^{86}Sr$ on igneous litholgoies and their metamorphic equivalents, because they are predominantly made of silicate minerals which are more resistant to weathering processes such as leaching (Faure, 1986, p.183ff).

There are still many areas of Britain where biosphere $^{87}Sr/^{86}Sr$ data is sparse, but ultimately this is being improved by the production of an interactive multi-isotope map of Britain by Evans *et al.* (in prep; Evans, *pers.com*.). To characterize the high $^{87}Sr/^{86}Sr$ biospheres of Britain further, the collection of more biosphere proxies from the following areas are recommended: on the Precambrian Dalradian Supergroup and igneous intrusions in the Northern Highland terrane of Scotland (see Figure 5.3 in chapter 5 for location of terranes); on and around the granitic rocks of late Silurian to early Devonian Argyll suite (chapter 5, section 5.1.3) and around the Cairngorm suite in the Grampian terrane of Scotland, particularly as thermal aureoles from these igneous intrusions may result in high biosphere $^{87}Sr/^{86}Sr$ >0.714 at elevations suitable for growing crops and grazing animals (chapter 8, section 8.1.2); on the Silurian and Devonian bedrock along the Welsh border between England and Wales, near to where several archaeological humans and animals with $^{87}Sr/^{86}Sr$ >0.714 have been excavated, from sites at Medieval Hereford (Evans *et al.,* 2012) and Roman Worcester (Montgomery *et al.,* unpublished report) in England and at Neolithic Ty Isaf and Penywyrlod in south Wales (Neil *et al.,* 2017).

Finally, it is recommended that when using Sr-isotope analysis in archaeological migration and mobility studies, if budgets allow, biosphere proxies should be collected on and around the chosen site or sites in question, rather than relying only on the preliminary Sr-isotope biosphere map of Britain produced by Evans *et al.* (2010). From the experience in this thesis, plant samples are easy to collect during geochemical surveys, requiring no specialised training or equipment, they are easy to store and the development of microwave assisted digestion by Warham (2011, p.42) has reduced thetime taken to chemically prepare the samples ready for analysis by TIMS. Ultimately, any biosphere$^{87}Sr/^{86}Sr$ data collected and published for Britain will go on to further improve the interactive multi-isotope map of Britain being produced by Evans *et al.* (in prep; Evans, *pers.com*.), which in turn will be useful to many academic disciplines, including archaeology.

Appendices

Appendix 1. Glossary

aphyric: an igneous rock texture with an absence of phenocrysts.

batholith: a very large igneous intrusion (>100km^2) that forms from cooled magma deep in the Earth's crust. Usually compromises of coarse-grained igneous rocks, such as granite and granodiorite.

bioaccessible: a substance that is able to come into contact with and be absorbed by an organism.

biosphere: the regions of the surface and atmosphere of the Earth occupied by living organisms.

calcareous: containing calcium carbonate; chalky.

diagenetic: the process of chemical and physical change in deposited sediment during its conversion to rock.

equigranular: a rock texture which is characterized by crystals of nearly the same size.

facies: the character of a rock expressed by its formation, composition, and fossil content.

felsic: igneous rocks, or metamorphic equivalents, that are enriched in the lighter elements such as silicon, oxygen, aluminium, sodium, and potassium, and are therefore rich in minerals such as feldspar and quartz.

heterogeneous: non-uniform in composition or character.

homogenous: uniform in composition or character.

inlier: an area of older rocks surrounded by younger rocks.

lenticular: a formation with a lens-shaped cross-section.

leucocratic: a rock composed mainly of light-coloured minerals.

lithic: a sedimentary or volcanic rock containing a large proportion of debris from previously formed rocks.

lithology: the general physical characteristics of a rock or rocks.

lithostratigraphy: the study of strata or rock layers, focusing mainly on geochronology, comparative geology, and petrology.

mafic: igneous rocks, or metamorphic equivalents, that are enriched in the elements magnesium and iron and are therefore rich in minerals such as olivine, pyroxene, amphibole, and biotite.

megacyrst: a crystal or grain that is considerably larger than the encircling matrix.

micaceous: a rock that is rich in mica minerals.

orogeny: an event that leads to a large structural deformation of the Earth's lithosphere (crust and upper most mantle) due to the interaction between tectonic plates.

phenocryst: a large or conspicuous crystal in a porphyritic rock, distinct from the groundmass.

pluton: an igneous intrusion that forms from cooled magma below the Earth's surface. In practice, "pluton" usually refers to a distinctive mass of igneous rock, typically several km^2 in dimension.

porphyritic: a rock texture containing distinct crystals or crystalline particles embedded in a compact groundmass.

pyroclastic: clastic rocks composed solely or primarily of volcanic materials.

suite: a group of igneous units with common textural, mineralogical and compositional characteristics.

terrane: a large proportion of crustal geology that is exotic with respect to the geology either side of it.

turbiditic: a sedimentary deposit formed by a turbidity current.

ultramafic: igneous rocks, or metamorphic equivalents, with very low silica content (<45%) and are usually composed of >90% mafic minerals.

unconformity: gaps in the geologic record that may indicate episodes of crustal deformation, erosion, and sea level variations.

volcaniclastic: clastic sediments composed mainly of particles of volcanic origin, regardless of how the sediment formed.

xenolith: a fragment of rock differing in origin, composition, structure, etc, from the igneous rock enclosing it.

Appendix 2. Geochemical Survey Field-notes

Field-notes from England and Wales

Field-notes of the plant $^{87}Sr/^{86}Sr$ collected from across Burbage common and woods (Leicestershire, England) on the 13/08/16 to 15/08/16.

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50000 Sheet
BW L1	0.71243	Triassic Sedimentary rocks, mainly mudstone.	The Mercia Mudstone Group	Anglian deposits; Wolston Clay and Thrussington Till mainly	52 32 38.4864N	1 20 0.7548W	Burbage Woods	Woodland	Oak, Ash and Hornbeam leaves		169
BW L2	0.71100	Triassic Sedimentary rocks, mainly mudstone.	The Mercia Mudstone Group	Anglian deposits; Wolston Clay and Thrussington Till mainly	52 32 54.204N	1 20 12.3648W	Burbage Common	Common	Oak, Willow and Sallow (?) leaves.		169
BW L3	0.71211	Triassic Sedimentary rocks, mainly mudstone.	The Mercia Mudstone Group	Anglian deposits; Wolston Clay and Thrussington Till mainly	52 33 9.3492N	1 20 24.1656W	Burbage Common	Common	Oak and Birch leaves.		169
BW L4	0.71186	Triassic Sedimentary rocks, mainly mudstone.	The Mercia Mudstone Group	Anglian deposits; Wolston Clay and Thrussington Till mainly	52 32 57.05N	1 20 36.46W	Burbage Woods	Woodland	Hornbeam and Field Maple leaves.	Near to stream.	169
BW L5	0.71019	Triassic Sedimentary rocks, mainly mudstone.	The Mercia Mudstone Group	Anglian deposits; Wolston Sand and Gravel, Wolston Clay and Thrussington Till	52 31 52.2084N	1 19 14.88W	Aston Flamville, Hinckley	Village and arable land	Ash, Lime and Hawthorn leaves.		169

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50000 Sheet
BW L6	0.71170	Triassic Sedimentary rocks, mainly mudstone.	The Mercia Mudstone Group; The Penarth Group	Anglian deposits; Dunsmore Gravel, Wolston Sand nd Gravel, Thrussington Till and Peat	52 26 2.88N	1 18 9.93W	Pailton, Rugby	Mixed Farmland	Sycamore, Field Maple and Elm leaves.		169

Field-notes for the plant $^{87}Sr/^{86}Sr$ collected from across Charnwood Forest (Leicestershire, England) on the 17/03/14 to 19/03/14.

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Deposits	Latitude	Longitude	Location	Setting	Plants	Site Description	BGS 1:50000 Sheet
CHW01	0.71098	Ordovician, Granodiorite, diorite and gabbro.	Mountsorrel Igneous Complex	Holocene head deposits	52 43 36.80N	1 10 18.22W	Buddon Woods, Kinchley Lane.	Roadside, Active Quarry and Reservoir nearby.	Oak, dried leaves & twigs	Directly rooted into exposed rock.	155
CHW02	0.71079	Precambrian, Volcaniclastic sedimentary rocks.	The Charnian Supergroup; Maplewell Group: The Brand Group	Holocene head deposits	52 43 19.2396N	1 12 51.462W	St Paul's Church, Woodhouse Eaves.	Church Garden, within a village.	Leaves of a well rooted annual plant	Directly rooted into exposed rock.	155
CHW03	0.71064	Precambrian, Volcaniclastic sedimentary rocks.	The Charnian Supergroup; Maplewell Group	Holocene head deposits	52 43 29.4744N	1 14 52.314W	Near Beacon Road.	Off from roadside, arable land close by.	Leaves of a Mature Holly tree	No exposed bedrock.	155

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Deposits	Latitude	Longitude	Location	Setting	Plants	Site Description	BGS 1:50000 Sheet
CHW04	0.71060	Precambrian, Volcaniclastic sedimentary rocks.	The Charnian Supergroup; The Blackbrook Group	Holocene head deposits. Anglian Oadby Till Memeber.	52 44 43.42N	1 15 41.97W	Off from Nanpantan Road, to the east.	Woodland on outcrop, arable land nearby.	Leaves of a Mature Holly tree	Exposed bedrock present, rhyolite.	155
CHW05	failed	Precambrian, Volcaniclastic sedimentary rocks.	The Charnian Supergroup; The Blackbrook Group	Holocene head deposits. Anglian Oadby Till Member.	52 44 43.38N	1 15 42.55W	Off from Nanpantan Road, to the east.	Woodland on outcrop, arable land nearby.	Pine cones	Exposed bedrock present, rhyolite.	155
CHW06	0.71110	Precambrian, Volcaniclastic sedimentary rocks.	The Charnian Supergroup; The Blackbrook Group	Holocene head deposits. Anglian Oadby Till Memeber.	52 44 43.35N	1 15 42.85W	Off from Nanpantan Road, to the east.	Woodland on outcrop, arable land nearby.	Leaves from Grass & Bluebells	LJCHW06 taken from directly above exposed bedrock, believed to by rhyolite.	155
CHW07	0.71058	Precambrian Diorites	North Charnwood Diorites	Holocene head deposits. Anglian Oadby Till Memeber.	52 44 42.0036N	1 16 2.2584W	To the west of Nanpantan Road.	Woodland and grassland, arable land nearby.	Leaves from a Elderflower Sapling	No exposed bedrock.	155
CHW08	0.71040	Precambrian Diorites	North Charnwood Diorites	Holocene head deposits. Anglian Oadby Till Memeber.	52 44 42.07N	1 16 3.14W	To the west of Nanpantan Road.	Woodland and grassland, arable land nearby.	Old tree, possibly sycamore	No exposed bedrock.	155
CHW09	0.71063	Precambrian, Volcaniclastic sedimentary rocks.	The Charnian Supergroup; the Maplewell Group	Holocene head deposits	52 43 38.14N	1 18 55.47W	Off from Warren Hills Road.	Grassland with a sparse woodland.	Leaves of a Mature Holly tree	Exposed bedrock nearby.	155

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Deposits	Latitude	Longitude	Location	Setting	Plants	Site Description	BGS 1:50000 Sheet
CHW10	failed	Precambrian, Volcaniclastic sedimentary rocks.	The Charnian Supergroup; the Maplewell Group	Holocene head deposits	52 43 38.01N	1 18 55.67W	Off from Warren Hills Road.	Grassland with a sparse woodland.	Grass leaves	Exposed bedrock nearby.	155
CHW11	0.71039	Precambrian, Volcaniclastic sedimentary rocks.	The Charnian Supergroup; the Maplewell Group	Holocene head deposits	52 43 37.76N	1 18 55.91W	Off from Warren Hills Road.	Grassland with a sparse woodland.	Laurel leaves	Exposed bedrock nearby.	155
CHW12	failed	Precambrian, Volcaniclastic sedimentary rocks; Igneous rocks and tuffs	The Charnian Supergroup; The Maplewell Group; Whitwick volcanic complex	Holocene head deposits	52 44 54.10N	1 20 43.81W	Cademan Woods, Swanny-mote Road.	Woodland, arable land nearby.	Leaves of a Mature Holly tree	Exposed bedrock present.	141
CHW13	0.71118	Precambrian, Volcaniclastic sedimentary rocks; Igneous rocks and tuffs	The Charnian Supergroup; The Maplewell Group; Whitwick volcanic complex	Holocene head deposits	52 44 54.0528N	1 20 43.6344W	Cademan Woods, Swanny-mote Road.	Woodland, arable land nearby.	Fern Leaves	Exposed bedrock present. CHW13 taken from base of exposed rock.	141
CHW14	0.71060	Precambrian, Volcaniclastic sedimentary rocks; Igneous rocks and tuffs	The Charnian Supergroup; The Maplewell Group; Whitwick volcanic complex	Holocene head deposits	52 44 53.85N	1 20 43.03W	Cademan Woods, Swanny-mote Road.	Woodland, arable land nearby.	A shallow rooted unknown plant	Exposed bedrock present.	141
CHW15	0.71050	Precambrian, Volcaniclastic sedimentary rocks.	The Charnian Supergroup; The Maplewell Group: The Mercia Mudstone Group	Holocene head deposits	52 41 36.66N	1 12 11.14W	Coppice wood, Bradgate Park.	Woodland within a deer park.	Pine needles, twigs & cones	Exposed bedrock present.	155

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Deposits	Latitude	Longitude	Location	Setting	Plants	Site Description	BGS 1:50000 Sheet
CHW16	0.71047	Precambrian, Volcaniclastic sedimentary rocks.	The Charnian Supergroup; The Maplewell Group: The Mercia Mudstone Group	Holocene head deposits	52 41 40.02N	1 12 15.2892W	Coppice wood, Bradgate Park.	Woodland within a deer park.	Reed (?) leaves	Exposed bedrock present.	155
CHW17	0.71219	Triassic, Sedimentary rocks, mainly mudstone.	The Mercia Mudstone Group	Holocene head deposits	52 42 5.4828N	1 12 3.618W	Swithland Wood, Roecliffe Road.	Woodland, arable land nearby.	Leaves of a Mature Holly tree	No exposed bedrock	155
CHW18	0.71209	Triassic, Sedimentary rocks, mainly mudstone.	The Mercia Mudstone Group	Holocene head deposits	52 42 5.1228N	1 11 56.6412W	Swithland Wood, Roecliffe Road.	Woodland, arable nearby.	Laurel leaves	No exposed bedrock	155
CHW19	0.71142	Triassic, Sedimentary rocks, mainly mudstone.	The Mercia Mudstone Group	Holocene head deposits	52 42 4.65N	1 11 57.58W	Swithland Wood, Roecliffe Road.	Woodland, arable nearby.	Fern Leaves	No exposed bedrock	155

Field-notes of the mixed plant samples collected and their $^{87}Sr/^{86}Sr$ from around Church Stretton, Shropshire, England (near the Wales Border) on the 09/09/15 to 10/09/15.

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Altitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
CS L1	0.71220	Ordovician Sedimentary rocks	Arenig Series; Stiperstones Quartzite Formation, the Mytton Flags Formation	Devensian Till deposits	52 31 24.2 N	2 59 48.5W	188m	Near to the village Snead	Woodland surrounded by pasturws	Sycamore and Oak leaves		165
CS L2	0.71406	Ordovician Felsic tuff; sedimentary rocks	Arenig Series; Hyssington Volcanic Member interbedded with un-named grey mud and siltstones	Devensian Till deposits	52 32 33.7N	3 00 22.1W	255m	Towards Hyssington, off from the A488	Wooded area surrounded by pastures	Holly, Sycamore and Beech leaves		165
CS L3	0.71524	Precambrian Sedimentary rocks	Longmyndian; Wentor Series, Bridges Group	Head deposits, near Till deposits	52 32 19.5N	2 54 45.5W	215m	North of Wentor	Tree verge of mixed farmland	Hazel, Holly and Alder (?) leaves	Near to big stream, possible igneous dykes	166
CS L4	0.71147	Precambrian Sedimentary rocks	Longmyndian; Wentor Series, Bridges Group	Head deposits, near Till deposits	52 33 44.0N	2 53 36.7W	163m	Near to Bridges, near to Ratlinghope	Wooded area, mixed farmland	Littleleaf Linden (?), Sycamore and Holly	River nearby	166
CS L5	0.71248	Carboniferous Sedimentary rocks (including coal, ironstone and ferricrete)	Halesowen Formation	River Terrace deposits and Glaciofluvial gravels	52 36 57.3N	2 48 40.3W	122m	Over 1km south-west of Stapleton (SY5 7AL)	Woodland surrounded by mixed farmland	Common Alder (?) and Ash leaves	Near to pond	152

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Altitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
CS L6	0.71374	Carboniferous Sedimentary rocks (including coal, ironstone and ferricrete)	Halesowen Formation	Till deposits	52 34 43.8N	2 45 38.0W	153m	Near to Leebotwood	Wooded area surrounded by arable farmland	Oak, Dogwood and Leylandii (?) leaves		152
CS L7	0.70942	Silurian Sedimentary rocks	Wenlock Series; mainly Wenlock Shales	Till deposits and Alluvium	52 30 59.2N	2 42 42.3W	200m	Rushberry	Wooded area surrounded by arable farmland	Leylandii and Sycamore leaves	The Sycamore leaves around this area all looked ill	166
CS L8	0.71143	Precambrian Igneous Felsic rocks	Uriconian; North Hill Dacites and Unnamed Rhyolites	Near to Glacial sand and gravels	52 32 19.3N	2 43 39.8W	223m	Near to Store acton farm (road off B471)	Tree verge of mixed farmland, near to farm	Willow, Oak and Ash leaves		166
CS L9	0.71246	Ordovican Sedimentary rocks	Caradoc Series	Near Till deposits	52 33 19.9N	2 43 43.8W	228m?	Cardington	Tree verge of arable farmland	Ash and Elder (?) leaves		166
CS L10	0.71183	Precambrian Igneous Lava and tuff	Uriconian; Unnamed tuffs and basalts and the Middle Hill Andesites Dacites	Near to Till and Glacial sand and gravels	52 31 53.8N	2 47 02.7W	255m	Hope Bowdler	Tree verge of mixed farmland	Oak, Ash and Sycamore leaves		166
CS L11	0.71161	Precambrian Igneous Lava and tuff	Uriconian; Cwms Rhyolites and Ragleth Tuffs?	Till deposits	52 33 47.2N	2 45 57.3W	197m	Near to Comley, which is west of Enchmarsh	Wooded area surrounded by arable farmland	Hazel, Leylandii and Holly leaves		166
CS L12	0.71536	Ordovician Sedimentary rocks	Caradoc Series	Near Till deposits	52 30 14.9N	2 48 51.6W	216m	Scott Acton	Woodland surrounded by mixed farmland	Horse Chesnut, Holly and Dogwood leaves		166

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Altitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
CS L13	0.71158	Precambrian Sedimentary rocks	Longmyndian; Stretton Series, Stretton Shale Group	Possible Alluvium?	52 33 16.5N	2 48 21.5W	222m	All Stretton	Wooded area on outskirt of village, surrounded by pastures	Elder (?), Elm and Oak leaves	Near to stream.	166

Field-notes of the mixed plant samples collected and their $^{87}Sr/^{86}Sr$ from across the Forest of Dean, Gloucestershire (near the Wales border) on the 08/09/2015.

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Altitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
FOD L1	0.71059	Devonian Sedimentary rocks	Old Red Sandstone; Brownstones Formation	Near to a small amount of Head deposits and Alluvium	51 54 55.2N	2 30 23.7W	109m	To the east of Bromsash	Tree verges in and around village, arable farmland	Ash, Sycamore and Elder (?) leaves		215
FOD L2	0.71125	Devonian Sedimentary rocks	Old Red Sandstone; Brownstones Formation	Near to a small amount of Alluvium	51 52 38.1N	2 32 47.0W	71m	North of Hope Mansell	Tree verges in and around village, arable farmland	Maple, Oak and Ash leaves	Near to a stream	233

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Altitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
FOD L3	0.71580	Carboniferous Sedimentary rocks (including coal, ironstone and ferricrete)	South Wales Coal Measures Group; Pennant Sandstone Formation	none	51 49 52.7N	2 33 25.3W	150m	Great Berry Quarry, Brierley	Woodland in old disused quarry	Beech, Aspen (?) and Oak leaves	Plants directly rooted into rock	233
FOD L4	0.71166	Carboniferous Sedimentary rocks (including coal, ironstone and ferricrete)	South Wales Coal Measures Group; Pennant Sandstone Formation	none	51 48 40.6N	2 35 39.4W	244m	Approximately east of Berry Hill and Mile End	Woodland	Sweet Chesnut (?), Oak and Beech leaves		233
FOD L5	0.71020	Carboniferous Limestone with some suboridnate sandstone and shale	Carboniferous Limestone Series	none	51 47 32.1N	2 38 38.9W	112m	South-west of Scowles	Wooded area, arable farmland and quarry nearby	Hazel, Lime nd Sycamore leaves		233
FOD L6	0.71061	Devionian Sedimentary rocks	Old Red Sandstone; Tintern Sandstone Group	none	51 47 39.7N	2 40 09.3W	75m	Upper Redbrook	Wooded area in village	Birch, Sycamore and Hazel leaves	Near to a large stream	233
FOD L7	0.71329	Sedimentary rocks	Old Red Sandstone; St. Maughan's Group	Near to Alluvium and River Terrace deposits	51 47 45.9N	2 45 06.3W	68m	Just past Wonastow	Old Tree verge, arable farmland	Oak, Horese Chesnut and Field Maple leaves		233
FOD L8	0.71044	Carboniferous Limestone with some suboridnate sandstone and shale	Carboniferous Limestone Series	none	51 45 18.1N	2 36 27.0W	162m	South-east of Trow Green	Tree verge, arable farmland	Sycamore, Horse Chesnut and Oak leaves		233
FOD L9	0.71237	Carboniferous Sedimentary rocks (including coal, ironstone and ferricrete)	South Wales Coal Measures Group; Pennant Sandstone Formation	Near to Alluvium and River Terrace deposits	51 46 05.6N	2 33 38.7W	61m	Parkend	Wooded area within village, and surrounding woodland	Aspen (?), Beech and Oak leaves		233

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Altitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
FOD L10	0.71169	Silurian Sedimentary rocks	Old Red Sandstone; St. Maughan's Group	Near to Alluvium and River Terrace deposits	51 45 31.2N	2 28 54.0W	32m	South-west of Blakeney	wooded area near village surrounded by arable farmland	Alder (?), Birch and Beech leaves	Near to a large stream	233
FOD L11	0.71213	Devionian Sedimentary rocks	Old Red Sandstone; Brownstones Formation	Near Alluvium	51 47 28.6N	2 29 13.1W	107m	East of Soudley	Woodland just outside of village	Hazel, Ash and Sweet Chesnut (?) leaves	Near to a large stream	233
FOD L12	0.71029	Carboniferous Limestone with some suboridnate sandstone and shale	Carboniferous Limestone Series	none	51 47 59.5N	2 30 28.8W	133m	Ruspidge	Woodland in small disused quarry just outside village	Hornbeam, Leylandii and Birch leaves		233

Field-notes of the mixed plant samples collected and their $^{87}Sr/^{86}Sr$ from around the Stanner-Hanter Complex, Kington, Herefordshire, England (near the Wales border) on the 09/09/2015.

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Deposits	Latitude	Longitude	Altitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
SHCL1	0.71314	Silurian Sedimentary rocks.	Undifferent-iated Wenlock and Ludlow Strata.	Near Alluvium	52 12 15.3N	3 03 11.7W	245m	Past Kington, off from Ridgebourne Road.	Wooded area next to mixed farmland.	Hornbeam, Beech and Alder leaves.	Below Hill of Stanner-Hanter Complex.	197
SHCL2	0.71192	Precambrian Igneous rocks	Stanner-Hanter Complex: Dolerite and Granophyric Granite	Glacio-fluvial Sheet deposits	52 12 47.2N	3 05 39.7W	192m	Off from Hanter Lane, Burlingjobb.	Tree verge of mixed farmland, close to private woodland.	Elder, Leylandii and Hawthorn leaves		197
SHCL3	0.71270	Precambrian Igneous rocks	Stanner-Hanter Complex: Dolerite and Gabbro	Near Alluvium	52 13 14.6N	3 05 03.8W	211m	Off from the A44, towards Walton.	Woodland, arable land.	Elm and Hornbeam leaves.	Below Hill of Stanner-Hanter Complex.	197
SHCL4	0.71220	Precambrian Sedimentary rocks.	Longmydian: Strinds Formation and Yat Wood Formation	Near Till deposits	52 13 28.3N	3 05 57.3W	234m	Old Radnor.	Tree verges within the village, quarry nearby and arable farmland.	Ash, Sweet Chesnut and Oak leaves.		197
SHCL5	0.71613	Silurian Sedimentary rocks.	Undifferent-iated Wenlock and Ludlow Strata.	Till deposits	52 14 07.32N	3 08 57.6W	261m	Near to New Radnor.	Woodland surrounded by mixed farmland.	Sallow?, Pine and Dogwood? leaves.		assumed from 197

Field-notes of the mixed plant samples collected and their $^{87}Sr/^{86}Sr$ from across the Lake District, Cumbria, England on the 09/01/15 and 18/07/15 to 19/07/15.

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Attitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50-000 Sheet
LD L1	0.71035	Ordovician Sedimentary rocks	Skiddaw Group; Kirkstile Formation	Near Till and Peat deposits	54 39 30N	03 13 42W	314ft	Near to Bassenth-waite Lake, roughly east of Embleton	Woodland	Fern, Ash and Hazel leaves	Lake nearby	29
LD L2	0.70968	Carboniferous Sedimentary rocks (including limestone) and Coal Measures	Yoredale Group; Hensing-ham Formation. Pennine Coal Measures; Upper Coal Measures	Glacio-fluvial, River Terrace and Peat deposits	54 36 04N	03 25 41W	354ft	In and around the village Ullock	Tree verge and wooded areas, mixed farmland	Sycamore, Ash and Alder (?) leaves	Just over 8km from coast	28
LD L3	0.70988	Ordovician Sedimentary rocks	Skiddaw Group; Buttermere Formation	Till and Glacio-fluvial Deposits	54 32 24N	03 26 14W	521ft	Just north of Kirkland	Tree verges, pastures	Sycamore, Crab Apple (?) and Ash leaves	Just over 5km from coast	28
LD L4	0.71002	Ordovician Sedimentary rocks	Skiddaw Group; Buttermere Formation	Till and Alluvium deposits	54 31 02N	03 27 02W	656ft	Just north of Ennerdale Bridge	Wood-land, pastures to west	Elder (?), Pine and Larch leaves	Just over 5km from coast, near a stream	28
LD L5	0.70960	Ordovician Igneous Tuffs (mafic) and Lava	Birker Fell Formation; Devoke Water Member and undivided lavas.	Near to Till and Peat deposits	54 29 39N	03 27 05W	958ft	Sallathwaite Wood	Woodland only	Unknown and Pine leaves	Just over 5km from coast	28

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Attitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50-000 Sheet
LD L6	0.70906	Triassic Sedimentary rocks	Sherwood Sandstone Group; Calder Sandstone Formation	Till deposits	54 25 29N	03 27 06W	390ft	North-west of Gosforth	Tree verges, mixed farmland	Hawthorne, Wild Cherry and Plum (?) leaves	Less than 5km from coast	37
LD L7	0.70944	Ordovician Igneous Lava (mafic)	Borrowdale Volcanic Group; Birker Fell Formation; undivided lavas mainly.	Till and Alluvium deposits	54 24 06N	03 22 41W	160ft	In and around the village Santon Bridge	Wooded areas, wood-land, pastures	Oak, Sycamore and Holly leaves		38
LD L8	0.71471	Ordovician-Silurian Igneous rock (felsic)	Eskdale Intrusion; Granite	Near River Terrace and Alluvium deposits	54 23 28N	03 17 23W	150ft	Beckfoot Quarry (Eskdale)	Trees within Quarry	Hazel and Birch leaves	Trees directly rooted in rock	38
LD L9	0.71053	Ordovician-Silurian Igneous rock (felsic)	Eskdale Intrusion; Granite	Till, River Terrace and Alluvium deposits	54 23 51N	03 14 01W	308ft	To the east of Boot	Tree verges and wooded area. pastures	Ash, Elder (?) and Sycamore leaves		38
LD L10	0.71036	Ordovicina Igneous Lava and Tuffs	Borrowdale Volcanic Group; Waberth-waite Formation, Birker Fell Formation (undivided lavas mainly)	Scree and Moraine deposits	54 24 57N	03 06 42W	1276ft	Wrynose Pass, west of Little Langdale	Heath-land (?), Barren Hilltop	Mixed Reed leaves		38
LD L11	0.70955	Ordovician Igneous Tuffs and volcaniclastic Sedimentary rocks	Borrowdale Volcanic Group; Lincomb Tarns Formation, Seath-waite Fell Formation	Till and Alluvium deposits	54 26 28N	02 58 23W	226ft	Between Ambleside and Rydal	Wood-land (?) and wooded areas, mixed farmland	Oak, Fern and Ash leaves		38

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Attitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50-000 Sheet
LD L12	0.71221	Ordovician Igneous Tuffs and volcaniclastic Sedimentary rocks	Borrowdale Volcanic Group; Lincomb Tarns Formation, Seath-waite Fell Formation	Till, Moraine, Head and Alluvium deposits	54 30 25N	03 02 38W	643ft	Near to southern Thirlmere Lake	Wood-land and Wooded areas	Hazel, Larch and Aspen leaves	Near to lake	29
LD L13	0.70990	Ordovician Igneous Lava and Tuffs	Borrowdale Volcanic Group; Birker Fell Formation	Till and Peat deposits	54 34 59N	03 05 19W	544ft	North-west of Thirlmere Lake, just south of Naddle	Tree verges, wooded area, pastures	Hazel, Sycamore and Ash leaves		29
LD L14	0.71227	Ordovician Sedimentary rocks	Skiddaw Group; Buttermere Formation, Kirkstile Formation	Till and Alluvium deposits	54 35 59.41N	03 9 0.85W		Surrounding the market town of Keswick	Wooded areas and woodland surrounding lake	Grey Willow and Hawthorne leaves	Near to Lake	29
LD L15	0.71185	Silurian Sedimentary rocks	Winder-mere Supergroup; Coniston Group; Bannisdale Formation	Possible Till and Alluvium deposits	54 21 37N	02 56 14W		Windermere Lake	Wooded area on lake islands	Unknown and Oak leaves	Near to Lake	38
LD L16	0.71069	Ordovician Sedimentary rocks	Skiddaw Group; Hope Beck Formation, Lowes-water Formation.	Till, Scree and Peat deposits	54 36 36N	03 15 12W	925ft	Off from Whinlatter Pass, west of Thornth-waite	Wood-land	Pine and Grey Willow leaves	Near a stream	29
LD L17	0.71298	Ordovician-Silurian Felsic Rock/Eskdale Granite	Eskdale Intrusion; Coarse-grained Granite	River Terrace and Alluvium deposits	54 23 1.97N	03 18 41.36W		South-east of the village Eskdale Green	Wooded areas, mixed farmland	Holly, Conifer and Fir (?) leaves	Near a river	38

Field-notes for each 1km^2 box and their $^{87}Sr/^{86}Sr$ from across the Malvern Hills. The latitude and longitude represent the approximate centre of each 1km^2 box

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Deposits	Latitude	Longitude	Location	Setting	BGS 1:50 000 Sheet
MB1 A	0.71145	Silurian Sedimentary rocks (including Limestone)	Wenlock Shale and Limestone, Lower Ludlow Shale	Possible Head deposits	52 02 26.33N	2 25 15.21W	In and around Ledbury	Woodland, Farmland and Housing Estate	216
MB1 B	0.70991	Silurian Sedimentary rocks (including Limestone)	Wenlock Shale and Limestone	Possible Head deposits	52 02 26.33N	2 25 15.21W	In and around Ledbury	Woodland, Farmland and Housing Estate	216
MB2 A	0.71032	Silurian Sedimentary rocks (including Limestone)	May Hill Sandstone, Wenlock Shale and Limestone	Possible Head deposits	52 02 39.83N	2 24 22.77W	North-east of Ledbury	Farmland	216
MB2 B	0.709725	Silurian Sedimentary rocks (including Limestone)	May Hill Sandstone, Wenlock Shale and Limestone	Possible Head deposits	52 02 39.83N	2 24 22.77W	North-east of Ledbury	Farmland	216
MB3 A	0.70974	Silurian Sedimentary rocks (including Limestone)	Wenlock Limestone, Aymestry Limestone, Upper Ludlow Shale and Lower Old Red Sandstone	none	52 02 20.57N	2 23 46.87W	North-west of Eastnor	Woodland, Farmland and Housing Estate	216
MB3 B	0.70985	Silurian Sedimentary rocks (including Limestone)	Wenlock Limestone, Aymestry Limestone, Upper Ludlow Shale and Lower Old Red Sandstone	none	52 02 20.57N	2 23 46.87W	North-west of Eastnor	Woodland, Farmland and Housing Estate	216

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Deposits	Latitude	Longitude	Location	Setting	BGS 1:50 000 Sheet
MB4 A	0.71041	Silurian Sedimentary rocks (including Limestone)	Wenlock Limestone ,Aymestry Limestone and Upper Ludlow Shale	Near to Head deposits	52 01 39.71N	2 23 24.66W	In and around Eastnor	Village, Castle Estate and Farmland	216
ML4 B	0.71041	Silurian Sedimentary rocks (including Limestone)	Wenlock Limestone ,Aymestry Limestone and Upper Ludlow Shale	Near to Head deposits	52 01 39.71N	2 23 24.66W	In and around Eastnor	Village, Castle Estate and Farmland	216
MB5 A	0.71212	Silurian Sedimentary rocks	Wenlock Limestone, Lower Ludlow Shale, Aymestry Limestone and Upper Ludlow Shale	Head deposits and possible Alluvium	52 01 46.67N	2 22 25.94W	East of Eastnor	Deer park, Farmland and Wooded areas	216
MB5 B	0.71132	Silurian Sedimentary rocks	Wenlock Limestone, Lower Ludlow Shale, Aymestry Limestone and Upper Ludlow Shale	Head deposits and possible Alluvium	52 01 46.67N	2 22 25.94W	East of Eastnor	Deer park, Farmland and Wooded areas	216
MB6 A	0.71203	Cambrian-Ordovician Sedimentary rocks	Bronsil Shale; May Hill Sandstone	Head deposits	52 01 45.26N	2 21 27.80W	West of Hollybush	Farmland and Woodland	216
MB6 B	0.71286	Cambrian-Ordovician Sedimentary rocks	Bronsil Shale; May Hill Sandstone	Head deposits	52 01 45.26N	2 21 27.80W	West of Hollybush	Farmland and Woodland	216
MB7 A	0.71178	Triassic Sedimentary rocks	Malvern Complex; Merica Mudstone Group	Near to River Terrace deposits	52 01 37.20N	2 20 29.00W	In and around Hollybush	Village, Woodland, Farmland and open grassland	216

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Deposits	Latitude	Longitude	Location	Setting	BGS 1:50 000 Sheet
MB7 B	0.71211	Triassic Sedimentary rocks	Malvern Complex; Merica Mudstone Group	Near to River Terrace deposits	52 01 37.20N	2 20 29.00W	In and around Hollybush	Village, Woodland, Farmland and open grassland	216
MB8 A	0.71108	Triassic Sedimentary rocks	Mercia Mudstone Group	River Terrace deposits, possible Head deposits and Alluvium	52 01 18.30N	2 19 24.49W	South-west of Birts Street	Farmland and open grassland	216
MB8 B	0.71076	Triassic Sedimentary rocks	Mercia Mudstone Group	River Terrace deposits, possible Head deposits and Alluvium	52 01 18.30N	2 19 24.49W	South-west of Birts Street	Farmland and open grassland	216
MB9 A	0.71346	Precambrian Igneous felsic and mafic rocks	Malvern Complex; May Hill Sandstone	Near to River Terrace deposits	52 02 09.25N	2 20 40.80W	Just north of Hollybush	Woodland	216
MB9 B	0.71347	Precambrian Igneous felsic and mafic rocks	Malvern Complex; May Hill Sandstone	Near to River Terrace deposits	52 02 09.25N	2 20 40.80W	Just north of Hollybush	Woodland	216
MB10 A	0.71310	Precambrian Igneous felsic and mafic rocks	Malvern Complex; May Hill Sandstone; Mercia Mudstone Group	Near to River Terrace deposits	52 02 43.34N	2 20 40.99W	Further north of Hollybush	Open grassland and woodland	216
MB10 B	0.71321	Precambrian Igneous felsic and mafic rocks	Malvern Complex; May Hill Sandstone; Mercia Mudstone Group	Near to River Terrace deposits	52 02 43.34N	2 20 40.99W	Further north of Hollybush	Open grassland and woodland	216

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Deposits	Latitude	Longitude	Location	Setting	BGS 1:50 000 Sheet
MB11 A	0.71178	Triassic Sedimentary rocks	Mercia Mudstone Group	River Terrace deposits	52 02 31.42N	2 19 37.43W	North-west of Castlemorton	Farmland and open grassland	216
MB11 B	0.71068	Triassic Sedimentary rocks	Mercia Mudstone Group	River Terrace deposits	52 02 31.42N	2 19 37.43W	North-west of Castlemorton	Farmland and open grassland	216

Further field-notes for each 1km^2 box (A and B repeats respectively) from across the Malvern Hills. Includes the latitude and longitude for each of the 3 locations visited within each 1km^2 and the type of plant collected, on the 10/07/14 to 12/07/14.

Plant Sample Code	Plant Location Number	Plant Description	Latitude	Longitude	Location	Setting	Sample Site Description
MB1 A	M20A	Oak	52 02 26.00N	2 25 01.65W	Upper Hall Estate on Upper Hall Farm (a road off the A449)	Farmland and woodland	Near a stream
	M32A	Silver Birch	52 02 09.76N	2 25 05.02W	Around No6 Horse Lane Orchard, Ledbury, Herefordshire (HR8 1PP)	Housing estate in Ledbury	
	M33A	Cherry Tree (?)	52 02 40.60N	2 25 02.23W	Dog Hill Woods, Ledbury	Woodland	
MB1 B	M20B	Sycamore	52 02 26.00N	2 25 01.65W	Upper Hall Estate on Upper Hall Farm (a road off the A449)	Farmland and woodland	
	M32B	Royal Purple' Cotinus coggygria	52 02 09.76N	2 25 05.02W	around No6 Horse Lane Orchard, Ledbury, Herefordshire (HR8 1PP)	Housing estate in Ledbury	

	M33B	Sycamore	52 02 40.60N	2 25 02.23W	Dog Hill Woods, Ledbury	Woodland
MB2 A	M19A	Sycamore	52 02 46.31N	2 24 39.86W	Side road off Cut throat lane, near a house named West Hill House	Farmland and countryside houses
	M21A	Dogwood (?)	52 02 44.54N	2 24 04.91W	Near Posterity, Lower Mitchell Barn, Worcester Road (A449), Ledbury, Herefordshire (HR8 1EG)	Farmland and nearby a train track (no longer in use?)
	M31A	Oak	52 2 33.17N	2 24 39.83W	Lay-by on A449 (Worcester Road)	Tree verge next to Farmland
MB2 B	M19B	Oak	52 02 46.31N	2 24 39.86W	Side road off Cut throat lane, near a house named West Hill House	Farmland and countryside houses
	M21B	Elm	52 02 44.54N	2 24 04.91W	Near Posterity, Lower Mitchell Barn, Worcester Road (A449), Ledbury, Herefordshire (HR8 1EG)	Farmland and nearby a train track (no longer in use?)

	M31B	Ash	52 2 33.17N	2 24 39.83W	Lay-by on A449 (Worcester Road)	Tree verge next to Farmland
MB3 A	M18A	Sycamore	52 02 15.56N	2 23 41.94W	Near Roger Oates Design Co Ltd, Eastnor, Ledbury (HR8 1EL)	Farmland and woodland
	M22A	Ivy	52 02 37.70N	2 23 59.59W	On side road near Posterity, Lower Mitchell Barn, Worcester Road (A449), Ledbury, Herefordshire (HR8 1EG), before joining the A438	Farmland and nearby a train track (no longer in use?)
	M23A	Poplar	52 02 00.51N	2 23 34.03W	Along Upper Road, Eastnor	Farmland and Hosing estate in Eastnor
MB3 B	M18B	Ivy	52 02 15.56N	2 23 41.94W	Near Roger Oates Design Co Ltd, Eastnor, Ledbury (HR8 1EL)	Farmland and woodland
	M22B	Hawthorn	52 02 37.70N	2 23 59.59W	On side road near Posterity, Lower Mitchell Barn, Worcester Road (A449), Ledbury,	Farmland and nearby a train track (no longer in use?)

					Herefordshire (HR8 1EG), before joining the A438		
	M23B	Brambles	52 02 00.51N	2 23 34.03W	Along Upper Road, Eastnor	Farmland and Hosing estate in Eastnor	
MB4 A	M17A	Sinningia (?)	52 01 55.96N	2 23 31.18W	Eastnor Church of England Primary School, Clencher's Mill Lane, Eastnor, Ledbury, Herefordshire (HR8 1RA)	Within the village of Eastnor	
	M24A	Rose bush	52 01 50.22N	2 23 32.08W	Clencher;s Mill Lane, Eastnor	Farmland and Eastnor Castle Estate	Dusty location
	M25A	Sycamore	52 01 40.07N	2 23 31.13W	near to Bubbles Nursery and Birchams Grange Residential Care Home Birchams Grange Eastnor Ledbury, Herefordshire (HR8 1RW)	Farmland, Eastnor castle Estate woodland	Dusty location, sycamore look poorly

MB4 B	M17B	Wild Cherry	52 01 55.96N	2 23 31.18W	Eastnor Church of England Primary School, Clencher's Mill Lane, Eastnor, Ledbury, Herefordshire (HR8 1RA)	Within the village of Eastnor	
	M24B	Sycamore	52 01 50.22N	2 23 32.08W	Clencher;s Mill Lane, Eastnor	Farmland and Eastnor Castle Estate	Dusty location
	M25B	Laurel	52 01 40.07N	2 23 31.13W	near to Bubbles Nursery and Birchams Grange Residential Care Home Birchams Grange Eastnor Ledbury, Herefordshire (HR8 1RW)	Farmland, Eastnor castle Estate woodland	Dusty location
MB5 A	M16A	Ivy	52 01 46.09N	2 22 10.00W	Near D3 Events Ltd, Bronsil House, Eastnor, Herefordshire (HR8 1EP)	Countryside houses, farm land and wooded areas	
	M26A	Oak	52 02 2.51N	2 22 42.10W	Eastnor Castle Deer Park (HR8 1RQ), near to Tinkers Grove cottage	Deer Park/common	

	M27A	Maple (?)	52 01 42.34N	2 22 33.10W	Unnamed road off the A438, near to a house named Westleigh	Countryside houses, farmland and wooded area
MB5 B	M16B	Ash (?)	52 01 46.09N	2 22 10.00W	Near D3 Events Ltd, Bronsil House, Eastnor, Herefordshire (HR8 1EP)	Countryside houses, farm land and wooded areas
	M26B	Birch	52 02 2.51N	2 22 42.10W	Eastnor Castle Deer Park (HR8 1RQ), near to Tinkers Grove cottage	Deer Park/common
	M27B	Horse Chesnut	52 01 42.34N	2 22 33.10W	Unnamed road off the A438, near to a house named Westleigh	Countryside houses, farmland and wooded area
MB6 A	M04A	Fern	52 01 46.55N	2 21 18.52W	Upper House Farm	On private road near farmhouse
	M05A	Ash (?)	52 01 37.89N	2 21 56.46W	Lay-by on A438	Woodland near main road
	M15A	Elm	52 01 52.05N	2 21 04.71W	Side road off A438, towards Peack Villa, Eastnor Castle, eastnor, Herefordshire	Farmland, woodland and small lake nearby

					(HR8 1ES)	
MB6 B	M04B	Sycamore	52 01 46.55N	2 21 18.52W	Upper House Farm	On private road near farmhouse
	M05B	Sycamore	52 01 37.89N	2 21 56.46W	Lay-by on A438	Woodland near main road
	M15B	Maple	52 01 52.05N	2 21 04.71W	Side road off A438, towards Peack Villa, Eastnor Castle, eastnor, Herefordshire (HR8 1ES)	Farmland, woodland and small lake nearby
MB7 A	M03A	Ash	52 01 40.65N	2 20 18.65W	All Saints Church, Hollybush	Near a graveyard and main road
	M06A	Alder	52 01 50.72N	2 20 41.82W	1st lay-by on road towards Gullet Quarry (HR8 1EU)	Woodland
	M28A	Sycamore	52 01 44.77N	2 20 27.10W	Side road off the A438 which connects to a private road	Open grassland to converts to farmland, woodland and two countryside houses

						nearby	
MB7 B	M03B	Poplar	52 01 40.65N	2 20 18.65W	All Saints Church, Hollybush	Near a graveyard and main road	
	M06B	Sallow (?)	52 01 50.72N	2 20 41.82W	1st lay-by on road towards Gullet Quarry (HR8 1EU)	Woodland	
	M28B	Ash	52 01 44.77N	2 20 27.10W	Side road off the A438 which connects to a private road	Open grassland to converts to farmland, woodland and two countryside houses nearby	
MB8 A	M01A	Hazel	52 01 1.09N	2 19 7.55W	The Duke of York Country Pub (WR13 6JQ)	Next to pub car park, stream and field of wild flowers	Potentially rooted into stream
	M02A	Sallow (?)	52 01 33.00N	2 19 24.23W	B4208, Coombe Green	Open grassland near two countryside homes	Rooted near private garden
	M30A	Oak	52 01 14.12N	2 19 40.59W	Pull-in off the A438 just after junction from the B4208	Tree verge next to Farmland	

MB8 B	M01B	Ash (?)	52 01 1.09N	2 19 7.55W	The Duke of York Country Pub (WR13 6JQ)	Next to pub car park, stream and field of wild flowers	
	M02B	Beech (?)	52 01 33.00N	2 19 24.23W	B4208, Coombe Green	Open grassland near two countryside homes	Rooted near private garden
	M30B	Ash (?)	52 01 14.12N	2 19 40.59W	Pull-in off the A438 just after junction from the B4208	Tree verge next to Farmland	
MB9 A	M07A	Laurel	52 01 59.61N	2 20 41.13W	2nd lay-by on road towards Gullet Quarry (HR8 1EU)	Woodland	
	M08A	Oak	52 02 11.11N	2 20 42.72W	3rd lay-by on road towards Gullet Quarry (HR8 1EU)	Woodland	
	M09A	Holly	52 02 23.44N	2 20 42.87W	Near ZephlR Lidar, The Old Barns, Fairoaks Farm, Hollybush, Ledbury, Herefordshire (HR8 1EU)	Woodland	
MB9 B	M07B	Alder (?)	52 01 59.61N	2 20 41.13W	2nd lay-by on road towards Gullet Quarry (HR8 1EU)	Woodland	

	M08B	Apple tree (?)	52 02 11.11N	2 20 42.72W	3rd lay-by on road towards Gullet Quarry (HR8 1EU)	Woodland	
	M09B	Alder (?)	52 02 23.44N	2 20 42.87W	Near ZephlR Lidar, The Old Barns, Fairoaks Farm, Hollybush, Ledbury, Herefordshire (HR8 1EU)	Woodland	Near stream, potenially rooted in stream
MB10 A	M10A	Fern	52 02 27.66N	2 20 29.21W	Swinyard Carpark, Castlemorton Common	Open grassland/common, near car park	
	M11A	Fern	52 02 35.25N	2 20 42.06W	Castlemorton Common	Open grassland/common	
	M29A	Fern	52 02 26.24N	2 20 44.50W	Private Road towards Gullet Quarry (HR8 1EU)	Woodland, Common and small lake nearby	
MB10 B	M10B	Oak	52 02 27.66N	2 20 29.21W	Swinyard Carpark, Castlemorton Common	Open grassland/common, near car park	
	M11B	Silver Birch	52 02 35.25N	2 20 42.06W	Castlemorton Common	Open grassland/common	

	M29B	Ash	52 02 26.24N	2 20 44.50W	Private Road towards Gullet Quarry (HR8 1EU)	Woodland, Common and small lake nearby	
	M12A	Silver Birch	52 02 40.45N	2 19 54.16W	Near to Brambles Living Farm (WR13 6LH)	Open grassland/common, near road	
MB11 A	M13A	Damson Tree	52 02 20.95N	2 19 43.41W	Towards Huntsbridge, Malvern, Worcestershire (WR13 6DA)	Farmland, common, countryside homes	
	M14A	Sallow (?)	52 02 42.95N	2 19 22.58W	Towards Eight Oaks, Castlmorton, Malvern, Worcestershire (WR13 6BU)	Farmland, common, countryside homes	
	M12B	Sallow (?)	52 02 40.45N	2 19 54.16W	Near to Brambles Living Farm (WR13 6LH)	Open grassland/common, near road	
MB11 B	M13B	Willow	52 02 20.95N	2 19 43.41W	Towards Huntsbridge, Malvern, Worcestershire (WR13 6DA)	Farmland, common, countryside homes	Rooted into stream
	M14B	Ash (?)	52 02 42.95N	2 19 22.58W	Towards Eight Oaks, Castlmorton, Malvern,	Farmland, common, countryside homes	

Worcestershire
(WR13 6BU)

Field-notes of the mixed plant samples collected and their $^{87}Sr/^{86}Sr$ from around Nuneaton, Warwickshire, England, on the 01/09/15 to 02/09/15.

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Altitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
NUN L1	0.71110	Triassic Sedimentary rocks.	The Mercia Mudstone Group; Arden Sandstone Formation	Anglian deposits; Wolston Clay and Thrussington Till	52 32 34.5N	1 20 06.21W	109m	Burbage woods	Woodland surrounded by mixed farmland.	Oak, Holly and Maple leaves		169
NUN L2	0.71140	Triassic Sedimentary rocks.	The Mercia Mudstone Group; Arden Sandstone Formation	Anglian deposits; Anker Sand and Gravel. Holocene Alluvium	52 32 03.09N	1 28 56.3W	58m	Caldecote	Small wooded area in village surrounded by farmland	Sycamore, Leylandii and Littleleaf Linden (?) leaves		169
NUN L3	0.70989	Precambrian-Cambrian Igneous Felsic Tuff; Sedimentary rocks	Caldecote Volcanic Formation; Hartshill Sandstone Formation	Nearby Anglian deposits; Anker Sand and Gravel. Holocene River terrace deposits.	52 32 58.0N	1 30 26.6W	96m	B411, Nuneaton Rd	Wooded area to west, near pub and agricultural land.	Leylandii, Zelkova and Buddleja leaves		169
NUN L4	0.71045	Cambrian Sedimentary rocks	Outwoods Shale Formation	Nearby Anglian Till deposits	52 32 40.4N	1 31 53.24W	112m	Oldbury Rd (east of Oldbury)	Woodland near to housing estate.	Oak, Holly and Little Linden leaves		169

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Altitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
NUN L5	0.71067	Carboniferous Sedimentary rocks (with ironstone and ferricrete).	Coal Measures; Lower and Middle Coal Measures.	Nearby Anglian Till deposits	52 32 41.1N	1 33 07.9W	171m	Oldbury Rd (west of Oldbury)	Woodland	Hawthorne, Sycamore and Maple leaves		169
NUN L6	0.71249	Carboniferous Sedimentary rocks.	Barren Measures; Whitacre Member	Anglian Till deposits	52 30 21.2N	1 31 56.4W	147m	B4102, Astley Lane	Tree verge surrounded by farmland.	Oak, Ash and Honeylocust (?) leaves	The oak tress in this area all looked a bit ill.	169
NUN L7	0.71035	Carboniferous Sedimentary rocks (with ironstone and ferricrete).	Coal Measures; Lower and Middle Coal Measures.	Anglian Glaciofluvial and Till Deposits	52 29 47.9N	1 28 18.5W	99m	Gipsy Lane, Griff	Wooded area near to main roads.	Hawthorne, Oak and Ash leaves		169
NUN L8	0.71032	Triassic Sedimentary rocks.	Sherwood Sandstone Group	Anglian deposits; Dunsmore Gravel, Oadby Till, Wolston Clay and Thrussington Till	52 28 54.4N	1 26 12.8W	112m	Mill Lane, Western in Arden	Tree verge surrounded by agricultural land and a housing estate.	Rowan, Horse Chesnut and Wild Cherry (?) leaves		169

Field-notes of the mixed plant samples collected and their $^{87}Sr/^{86}Sr$ from Sherwood Forest and surrounding farmland, Nottinghamshire, England, on the 14/07/16.

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Altitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
SF L1	0.71358	Triassic Sandstone and conglomerate interbedded	Sherwood Sandstone Group	Near Alluvium	53 12 15.6N	1 04 40.3W	29m	Sherwood Forest National Nature Reserve; crossroad for bridal path, central oak and major oak.	Forest	Mixed Oak leaves		113
SF L2		Triassic Sandstone and conglomerate interbedded	Sherwood Sandstone Group	Near Alluvium	53 12 10.4N	1 05 10.5W	102m	Sherwood Forest National Nature Reserve	Forest	Mixed Oak leaves		113
SF L3	0.71757	Triassic Sandstone and conglomerate interbedded	Sherwood Sandstone Group	Near Alluvium	53 12 28.51N	1 05 8.82W	55m	Sherwood Forest National Nature Reserve, nearest to plantation.	Forest	Mixed Oak leaves	Long horn cattle allowed to roam this part of forest.	113
SF L4	0.71218	Triassic Sandstone and conglomerate interbedded	Sherwood Sandstone Group	None	53 10 40.1N	1 05 40.8W	45m	Near Kings Clipstone, south-west of Edwinstowe.	Open land, tree verges around arable farmland	Mixed Hawthorn leaves		113
SF L5	0.70932	Triassic Sandstone and conglomerate interbedded	Sherwood Sandstone Group	None	53 05 42.8N	1 03 28.2W	78m	Around Longland Lane, south-west of Farnsfield	Around arable farmland	Ash, Sycamore, Elder (?) leaves		113

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Altitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
SF L6	0.70959	Triassic Sandstone and conglomerate interbedded	Sherwood Sandstone Group	Alluvium and near to a small Till deposit	53 21 58.8N	1 03 57.0W	30m	B6045, near Blyth	Open land, tree verges around arable farmland	Oak, Lime and Elm leaves		101
SF L7	0.70987	Triassic Sandstone and conglomerate interbedded	Sherwood Sandstone Group	Possible Alluvium and near Till deposit	53 18 40.7N	1 03 08.5W	55m	Osberton Hall and Park Farm	Around arable farmland and private estate	Oak and Beech Leaves		101
SF L8	0.71028	Triassic Sandstone and conglomerate interbedded	Sherwood Sandstone Group	None	53 14 42.2N	1 06 09.6W	41m	Along Limetree Avenune, past Carburton	Edge of a Woodland,/arable farmland	Mixed Lime Leaves	Near small lake	113

Field-notes of the mixed plant samples collected and their $^{87}Sr/^{86}Sr$ from the Wrekin, Shropshire, England, on the 11/09/2015.

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Altitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
WL1	0.71203	Cambrian Sedimentary rocks	Merioneth and Tremadoc Series, Comley Series.	Near to Till deposits.	52 40 36.7N	2 31 49.6W	6m?	Wrekin forest.	Woodland	Beech, Elm? And Horse Chesnut leaves.		152
WL2	0.71270	Precambrian Igneous felsic rocks and tuffs	Uriconian and a Precambrian Granophyric granitic intrusion	Near to Till deposits.	52 41 19.7N	2 31 28.9W	139m	Ercall Ln, edge of Wrekin forest.	Woodland	Oak and Holly leaves.	Near to the M54/A5.	152
WL3	0.71134	Carboniferous Sedimentary rocks (with conglomerates)	Pennine Coal Measure Group; Upper Coal Measures	Till deposits	52 41 15.9N	2 32 40.6W	119m	Near to Cluddley.	Tree verges surrounded by agricultural land.	Oak, Elm and Ash leaves		152
WL4	0.71175	Precambrian Igneous rocks and tuffs	Uriconian and Dolerite intrusions	Near to Till deposits.	52 40 28.95N	2 32 37.99W	293m	Wrekin trial, Wrekin forest.	Woodland	Beech and Ash leaves		152

Field-notes from Scotland

Field-notes of the mixed plant samples collected and their $^{87}Sr/^{86}Sr$ from across the Cairngorms National Park, Scotland. Roughly follows a transect off from the A93/A939 between Blairgowrie to Grantown-on-Spey. Collected on the 24/08/14 to 26/04/14.

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
SCOT L1	0.71267	Devonian Sedimentary rocks, with andesitic lavas?	Lower Old Red Sandstone: Arbuthnott-Garvock Group; Scone Sandstone Formation; Hatton Conglomerate Member; possibly Craighall Conglomerate Formation?	Glacio-fluvial deposits	56 35 55.0788N	3 19 20.2166W	Outside of Blairgowrie	Wooded areas near arable farmland	Ash, Hawthorne and Sycamore leaves	Near to a stream	56W
SCOT L2	0.71100	Devonian Sedimentary rocks with andesitic lavas	Lower Old Red Sandstone: Arbuthnott-Garvock Group; Craighall Conglomerate Formation	Till and Glacio-fluvial deposits	56 37 46.6896N	3 21 35.0892W	Off from the A93, near Netherton	Wooded area near arable farmland	Oak and Sycamore leaves		56W
SCOT L3	0.7109	Precambrian Meta-sediments	Southern Highland Group; Cairn Gibbs Psammite Formation	Till and Glaciofluvial deposits	56 39 8.5752N	3 23 50.1936W	Off from the A93, just north of the village Bridge of Cally	Wooded area on steep river slope (Black Water), mixed farmland nearby	Hornbeam, Beech and Fern leaves		56W

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
SCOT L4	0.71066	Precambrian Meta-morphised Igneous rock (mafic)	Southern Highland Group; Amphibolite, Hornblende Schist and Metagabbro	Till and Glaciofluvial deposits	56 42 39.89N	3 24 50.06W	Off from the A93, south of Dalrulzian	Tree verges and woodland near River Blackwater, mixed farmland surrounding.	Sycamore, Ash and Hornbeam leaves	Near and rooted in river (Black Water)	56W
SCOT L5	0.71151	Precambrian Meta-sediments	Southern Highland Group; Mount Blair Psammite and Pelite	Till and Glacio-fluvial and Alluvium deposits	56 44 33.13N	3 24 17.94W	Off from A93, south of Lair	Pine Woodland (plantation) surrounded by patures	Mixed Pine leaves	Near to the river Black Water (~200m)	56W
SCOT L6		Precambrian Meta-sediments	Argyll Group; Crinian Subgroup	Till and Glacio-fluvial and Alluvium deposits	56 46 3.50N	3 23 50.36W	Off from A93, Cairngorms National Park, near to Dalnaglar Castle	Trees on/near castle estate with open grassland/pastures	Beech, Lime and Horse Chesnut leaves	Pond close by, close to Southern Highland Group bedrock	56W
SCOT L7	0.70971	Precambrian Meta-sediments	Argyll Group; Easdale Subgroup; Ben Lawers Schist Formation mainly	Till and Glacio-fluvial and Alluvium deposits	56 48 18.42N	3 26 25.29W	Off from A93, Cairngorms National Park, around a house called Ar Dachaidh, The Binzean	Patch of trees surrounded by pastures (sheep)	Wild Cherry, Pine and Conifer leaves		56W
SCOT L8	0.70879	Precambrian Calcareous Meta-sediments	Appin Group; Blair Atholl Subgroup; Gleann Beag Schist Formation mainly	Till and Glacio-fluvial deposits	56 50 16.96N	3 26 40.99W	Off from A93, north of Spittal of Glenshee (~2km)	Valley slopes, grassland and heath-land	Heather and Fern Leaves	Near to stream and Drumlins, no trees just shrubs and low-lying plants	56W
SCOT L9	Failed	Precambrian Calcareous Meta-sediments	Appin Group; Blair Atholl and Ballachulish Subgroup mainly	Till deposits	56 53 11.55N	3 24 56.00W	Off from A93, Cairngorms National Park. Around the Cafe Cafaidh Ski Slope, Glenshee Ski Centre.	Valley slopes, grassland and heath-land	Heather and Pine Leaves	Sparse vegetation, near to a stream	65W

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
SCOT L10	0.71432	Precambrian Quartzite	Appin Group; Ballachulish Subgroup mainly	Till deposits	56 55 54.714N	3 25 00.6276W	Off from A93, Cairngorms National Park, Invercauld Estate (conservation area)	Walled woodland within valley	Scots Pine and Larch (?) Leaves		65W
SCOT L11	0.71292	Precambrian Quartzite	Appin Group; Ballachulish Subgroup mainly	Alluvium	56 59 0.54N	3 23 38.9511W	off from A93, Cairngorms National Park, south of Braemar	Woodland on valley slope	Birch, Silver Birch and Larch (?) Leaves	Near to a stream and bog-land	65W
SCOT L12	0.71262	Precambrian Meta-sediments	Grampian Group (undifferentiated)	Alluvium	57 00 48.5712N	3 23 38.652W	A93, Cairngorms National Park, just north of Braemar around Braemar Castle.	Wooded areas on castle estate	Rowan and Lime Leaves		65W
SCOT L13	0.71555	Silurian Igneous rock (felsic)	Lochnagar Granite	Till and Glacio-fluvial deposits	57 00 07.19N	3 19 33.68W	Off of A93, Tullich Road, east of Braemar	Extensive Woodland running parallel to the River Dee	Heather, Birch and Scots Pine Leaves		65E
SCOT L14	0.71064	Silurian Igneous rock (mafic)	Abergeldie Complex (diorite-granodiorite)	Alluvium	57 01 59.24N	3 12 34.78W	A93, Cairngorms National Park, Ballater, Aberdeenshire. Near to Balmoral Castle	Woodland running parallel to the River Dee	Sycamore, Larch (?) and Yew Leaves	Near to and rooted into a river	65E

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
SCOT L15	0.71281	Precambrian Meta-sediments	Argyll Group; Easdale Subgroup mainly. Undiffernent-iated Igneous Intrusion	Till deposits	57 02 24.23N	3 04 36.62W	Off of B976, Cairngorms National Park, west of Ballater	Extensive Woodland near Loch Ullachie	Ash, Silver Birch and Fir Leaves	Near lake	65E
SCOT L16	0.71487	Silurian Igneous rock (felsic)	Ballater Granite	Alluvium	57 03 09.51N	3 01 27.20W	Just north-east of Ballater, Cairngorms National Park	Woodland running alongside the River Dee	Fern, Yew and Silver Birch leaves	Near a stream	65E
SCOT L17	0.71136	Silurian Igneous rock (felsic)	Glen Gairn Granite	Alluvium	57 05 14.48N	3 11 12.50W	Off of A939, near Braenaloin, Cairngorms National Park	Little wooded area at bottom of valley, surrounded by open heath-land and pastures	Scots Pine and Birch leaves	Boggy ground, with exposed granitic geology and loose boulders, near to stream	65E
SCOT L18	0.71114	Silurian Igneous rock (felsic)	Glen Gairn Granite	Till deposits	57 06 21.72N	3 08 17.16W	Off of A939	Wooded areas on heath-land	Scots Pine and Heather leaves	Bee farm nearby, exposed granite	65E
SCOT L19	0.71007	Precambrian Calcareous Meta-sediments	Appin Group; Blair Atholl and Ballachulish Subgroup mainly	Till deposits and Alluvium	57 09 38.33N	3 10 5.49W	Off of A939, in and around Tor-na-haish, near River Don	Dense woodland of Fir trees	Mixed Fir leaves	Near to a river	75E
SCOT L20	0.71148	Precambrian Meta-sediments	Argyll Group; Islay Subgroup: Easdale Subgroup	none	57 10 22.29N	3 14 3.06W	Off of A939, Lecht Road, north-west of Corgarff	Open heath-land with walled woodland, some pastures	Larch/Cedar (?) and Heather leaves	Dead stream in the area	75E

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
SCOT L21	0.71465	Precambrian Meta-sediments	Argyll Group; Islay Subgroup; Ladders Hill Formation?	none	57 13 6.10N	3 15 58.26W	Off of A939, Lecht Road, east of Blairnamarrow	Walled woodland sloping down to valley bottom	Scots Pine and unknown fern-like leaves	Loose mudstone	75E
SCOT L22	0.70795	Precambrian Meta-limestone	Appin Group; Blair Atholl Subgroup; Inchory Limestone Formation	Till deposits, near to Peat	57 15 26.28N	3 24 3.14W	Off from A939, north-west of Tomintoul	Woodland and trees from a quarry site on top of a v-shaped valley	Mixed Sycamore leaves	On valley edge and rooted into geology/bedrock	75W
SCOT L23	0.71773	Precambrian Calcareous Meta-sediments	Appin Group; Ballachulish Subgroup mainly	Till deposits and Alluvium	57 16 19.7148N	3 26 18.1032W	Off from A939, east of Bridge of Brown	Walled woodland surrounded by heath-land and pastures	Noble Fir (?), Larch (?) and Heather leaves		75W
SCOT L24	0.71418	Precambrian Quartzite	Grampian Group; Cromdale Hills Quartzite Member	Till deposits	57 16 27.5088N	3 32 58.7112W	Off from A939, south of Lynemore	Walled woodland surrounded by heath-land and pastures	Rowan, Birch and Alder (?) leaves	Rooted into exposed bedrock, near to stream	75W
SCOT L25	0.71463	Orovician Igneous rock (felsic)	Grantown Pluton (varying granites)	Till deposits	57 20 6.86N	3 37 33.81W	Just outside of Grantown-on-Spey	Woodland near to pastures	Horse Chesnut, Ash and Cherry leaves		74E

Field-notes of the mixed plant samples collected and their $^{87}Sr/^{86}Sr$ from in and surrounding Chapeltown, Ballindalloch, Scotland. Collected on the 26/08/14.

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Age and Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
SCOT CTL1	0.71094	Devonian Sedimentary rocks (including conglomerates)	Lower Old Red Sandstone; Tomintoul Group; Conglass Sandstone Formation	Till deposits. Near Alluvium and Peat	57 15 40.76N	3 21 39.01W	Off from A939, north-east of Tomintoul, Cairngorms National Park	Extensive woodland plantation	Alder (?), Larch and Fir leaves		75W
SCOT CTL2	0.71656	Devonian Sedimentary rocks (including conglomerates)	Lower Old Red Sandstone; Tomintoul Group; Raebag Sandstone Formation	Till deposits. Near Alluvium and Peat	57 16 30.83N	3 19 07.40W	Off from B9008, west of Chapeltown	Woodland area owned by the crown, surrounded by heath-land	Fir and Scots Pine leaves		75W
SCOT CTL3	0.70999	Precambrian Calcareous Metasediments	Appin Group; Blair Atholl and Ballachulish Subgroup	Till deposits and Alluvium. Possible some Peat.	57 16 52.08N	3 16 58.05W	Just north-west of Chapeltown	Wooded area surrounded by pastures	Birch, Fir and Elderflower leaves	Near to a larger stream or little river	75E
SCOT CTL4	0.70844	Precambrian Metalimestone	Appin Group; Ballachulish Subgroup mainly	Till deposits and Alluvium.	57 16 23.41N	3 17 35.28W	Chapeltown	Chapel-town, surrounded by pastures	Sycamore, Poplar (?) and Rowan leaves	Near to Church and stream	75E
SCOT CTL5	0.71426	Precambrian Quartzite	Appin Group; Ballachulish Subgroup; Corryhabbie Quartzite Formation	Till deposits and Alluvium	57 17 41.07N	3 17 35.28W	North-west of Chapeltown, near to Knockandhu	Wooded areas, small woodland, surrounded by pastures	Birch, Silver Birch and Scots Pine leaves	Near to stream	75W

Field-notes of the mixed plant samples collected and their $^{87}Sr/^{86}Sr$ from the north of the Cairn Gorm mountain, mainly surrounding Glenmore and Aviemore, Cairngorms National Park, Scotland. Collected on the 27/08/14 to 28/08/14.

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
SCOT GL1	0.71225	Precambrian Meta-sediments	Grampian group; Nethybridge Formtion	Glacio-fluvial deposits and Alluvium	57 12 54.70N	3 46 01.70W	Off from B970, north of Boat of Garten, Cairngorms National Park	Wooded area surrounded by arable farmland	Rowan and Scots Pine leaves		74E
SCOT GL2	0.71671	Precambrian Meta-sediments	Grampian group; Coylum-bridge Formation	Till, Moraine, Glacio-fluvial deposits, with Peat nearby	57 10 06.25N	3 46 05.08W	Off from B970, east of Coylumbridge	Woodland with patches of heath-land	Mixed Scots Pine leaves	Near to a stream	74E
SCOT GL3	0.71820	Precambrian Meta-sediments	Grampian group; Coylum-bridge Formation	Till and Glacio-fluvial deposits and Alluvium	57 09 55.26N	3 40 25.94W	East of Glenmore, around Norweigen Lodge, Cairngorms National Park	Dense woodland on sloping hill	Scots Pine and Silver Birch leaves	Near to and rooted in stream, bottom of hill is Loch Morlich	74E
SCOT GL4	0.71360	Silurian Igneous rock (felsic)	Cairngorm Pluton (varying granites)	Head and Scree deposits	57 08 11.22N	3 40 16.56W	Up towards Cairn Gorm, Cairngorms National Park	Mountain-ous, sparse vegetation	Elm (?) and Scots Pine leaves	Near to a stream, exposed granitic geology	74E
SCOT GL5	0.71375	Precambrian Meta-sediments	Grampian group; Coylum-bridge Formation	Moraine, Glacio-fluvial deposits and Peat	57 09 57.45N	3 43 39.26W	West of Glenmore, Cairngorms National Park	Woodland next to river leaving Loch Morlich	Scots Pine, Sallow (?) and Silver Birch leaves	Near to Loch Morlich and river	74E
SCOT GL6	0.71556	Precambrian Meta-sediments	Grampian group; Grantown Formation	Near Moraine and Glacio-fluvial deposits	57 09 18.45N	3 49 28.14W	25 Grampian Road, Cairngorms National Park, Aviemore, Highland	woodland around Loch an Eilein	Silver Birch, Larch and Alder (?) leaves	Near to Loch an Eilein	74E

Plant Sample Code	$^{87}Sr/^{86}Sr$	Bedrock Lithology	Geological Group	Quaternary Superficial Geology	Latitude	Longitude	Location	Setting	Plant Description	Sample Site Description	BGS 1:50,000 Sheet
SCOT GL7	0.71303	Precambrian Gneissose Meta-sediments	Grampian group; Central Highland Migmatite Complex	Glacio-fluvial deposits and Alluvium	57 09 51.33N	3 50 04.94W	B9152, Cairngorms National Park, Aviemore, Highland. Near a house called 'The Polchar'.	wooded area near to private house and farmland?	Beech, Fir and Oak leaves		74E
SCOT GL8	0.71639	Silurian Igneous rock (felsic)	Monadhliath Pluton (varying granites)	Till and Moraine deposits mainly	57 12 16.76N	3 50 00.25W	Just outside of Aviemore, Cairngorms National Park	Wooded area on housing estate and further up the hill	Silver Birch and unknown leaves	Near to and rooted in a stream	74E
SCOT GL9	0.71197	Precambrian Meta-sediments	Grampian group; Corrieyairack Subgroup; Loch Laggan Psammite Formation	Glacio-fluvial deposits and Alluvium	57 08 15.98N	3 55 06.45W	Off of A9, just north-east of Kincraig	Wooded area surrounded by pastures (sheep)	Mixed Silver Birch leaves		74W

Appendix 3. Extra information for chapter 3: Materials and Methods

3.1 Preparation of the Cation Exchange Resin Columns

Preparation of the Dowex AG 50W-X12 resin columns

The Dowex AG 50W-X12 resin columns are first washed down with 50mL of 6M HCL, followed by 50mL of MQ water. Another 50mL of 6M HCL is added and then 15mL of 2.5M HCL is added and allowed to drain through. All the eluted solutions are collected in glass beakers and deposed of approximately. These columns are now ready for use for the chemical preparation described in chapter 3, section 3.3.2.

Preparation of the Sr-SPEC resin columns

The Sr-SPEC resin columns are removed from their Savillex© container and each is rinsed with approximately 2mL of MQ water. The columns are then placed in a labelled rack and 200uL of Sr-SPEC resin from a ~30mL dropper bottle (~8 drops) is added to each. These columns are then washed with 10mL of MQ water, which is repeated five times, followed by 10mL of 6M HCL, which is repeated 3 times. A further 2mL of MQ water is added to each column before being conditioned, twice, with 0.5mL of 2M HNO_3 (nitric acid). All the eluted solutions are collected in Savillex© beakers and deposed of approximately when needed. These beakers are cleaned themselves once preparation of the Sr-SPEC resin columns is complete (section 3.2 below). These Sr-SPEc resin columns now ready for use for the chemical preparation described in chapter 3, section 3.3.2.

3.2. Cleaning of Savillex© vessels and MARS microwave dissolution tubes before chemical preparation in chapter 3, section 3.3.1

Savillex© vessels

The Savillex© vessels_were first physically wiped down with lint-free wipes to remove any visible deposits. The tubes were then rinsed with deionised water, before 2mL of 6M HCL was added to each vessel and transferred to the hot plate (100^{o}C) for one hour, with lids screwed on loosely. These tubes were then removed, rinsed three times in deionised water and then a further 2mL of 6M HCl was added to each before again being transferred back onto the hot plate for one hour, with lids screwed on loosely. The vessels were removed and rinsed again three times and allowed to dry in a laminar flow hood.

MARS microwave dissolution tubes

The MARS microwave dissolution tubes were first physically wiped down with lint-free wipes to remove any visible deposits. The tubes were then rinsed with deionised water, before 10mL of Qz distilled 6M HCl was added to each before being transferred into the microwave system (CEM MARS Xpress Xtraction) and microwaved at 175^{o}C for 20 minutes using a slow ramp up. These tubes were then removed, rinsed three times in deionised water and then a further 10mL of Qz distilled 6M HCl was added to each before again being transferred into the microwave system and microwaved at 175^{o}C for 20 minutes using a slow ramp up. The tubes were removed and rinsed again three times and allowed to dry in a laminar flow hood.

3.3. Cleaning of Savillex© vessels before collection of Sr elute from Cation Exchange Resin Columns

The Savillex©_vessels are cleaned for further use in the chemical prepation in chapter 3, section 3.3.2, by adding 2mL of 6M HCL to each vessel and transferred to the hot plate (100^{o}C) for one hour. They are then rinsed with approximately 5mL of MQ water and returned to hot plate to dry down (~5-10 minutes). These are then ready to be placed under appropriate resin column to collect the Sr elute.

3.4. The international standard NBS 987

The international standard NBS 987 analysed over the period of this thesis produced a $^{87}Sr/^{86}Sr$ of 0.710254 ±0.00001 (n=146, 2SD).

Run	BatchText	$^{87}Sr/^{86}Sr$
Triton1-686	NBS987	0.710250
Triton1-690	NBS987	0.710256
Triton1-690	NBS987	0.710253
Triton1-690	NBS987	0.710255
Triton1-691	NBS987	0.710254
Triton1-691	NBS987	0.710254
Triton1-691	NBS987	0.710253
Triton1-691	NBS987	0.710252
Triton1-692	NBS987	0.710252
Triton1-692	NBS987	0.710255
Triton1-693	NBS987	0.710251
Triton1-700	NBS987	0.710254
Triton1-702	NBS987	0.710264
Triton1-702	NBS987	0.710263
Triton1-702	NBS987	0.710262
Triton1-707	NBS987	0.710250
Triton1-707	NBS987	0.710255
Triton1-707	NBS987	0.710251
Triton1-707	NBS987	0.710244
Triton1-707	NBS987	0.710260
Triton1-708	NBS987	0.710240
Triton1-708	NBS987	0.710258
Triton1-708	NBS987	0.710261
Triton1-711	NBS987	0.710252
Triton1-711	NBS987	0.710261
Triton1-711	NBS987	0.710249
Triton1-712	NBS987	0.710255
Triton1-712	NBS987	0.710256
Triton1-715	NBS987	0.710259
Triton1-715	NBS987	0.710257
Triton1-715	NBS987	0.710248
Triton1-716	NBS987	0.710249
Triton1-716	NBS987	0.710256
Triton1-716	NBS987	0.710254
Triton1-717	NBS987	0.710251
Triton1-717	NBS987	0.710246
Triton1-717	NBS987	0.710256
Triton1-718	NBS987	0.710264
Triton1-719	NBS987	0.710255
Triton1-719	NBS987	0.710258

Run	BatchText	$^{87}Sr/^{86}Sr$
Triton1-719	NBS987	0.710255
Triton1-724	NBS987	0.710250
Triton1-724	NBS987	0.710258
Triton1-725	NBS987	0.710252
Triton1-725	NBS987	0.710252
Triton1-725	NBS987	0.710245
Triton1-726	NBS987	0.710246
Triton1-726	NBS987	0.710256
Triton1-727	NBS987	0.710258
Triton1-728	NBS987	0.710256
Triton1-728	NBS987	0.710256
Triton1-728	NBS987	0.710254
Triton1-729	NBS987	0.710255
Triton1-729	NBS987	0.710242
Triton1-729	NBS987	0.710247
Triton1-730	NBS987	0.710255
Triton1-730	NBS987	0.710259
Triton1-730	NBS987	0.710254
Triton1-731	NBS987	0.710254
Triton1-731	NBS987	0.710253
Triton1-731	NBS987	0.710255
Triton1-732	NBS987	0.710260
Triton1-736	NBS987	0.710249
Triton1-736	NBS987	0.710254
Triton1-736	NBS987	0.710249
Triton1-737	NBS987	0.710258
Triton1-737	NBS987	0.710256
Triton1-738	NBS987	0.710249
Triton1-738	NBS987	0.710253
Triton1-739	NBS987	0.710267
Triton1-739	NBS987	0.710260
Triton1-742	NBS987	0.710254
Triton1-742	NBS987	0.710254
Triton1-742	NBS987	0.710248
Triton1-743	NBS987	0.710260
Triton1-743	NBS987	0.710258
Triton1-743	NBS987	0.710249
Triton1-744	NBS987	0.710251
Triton1-745	NBS987	0.710257
Triton1-745	NBS987	0.710263
Triton1-745	NBS987	0.710246
Triton1-746	NBS987	0.710254
Triton1-746	NBS987	0.710261
Triton1-746	NBS987	0.710268
Triton1-748	NBS987	0.710254

Run	BatchText	$^{87}Sr/^{86}Sr$
Triton1-752	NBS987	0.710247
Triton1-752	NBS987	0.710251
Triton1-753	NBS987	0.710254
Triton1-754	NBS987	0.710242
Triton1-754	NBS987	0.710253
Triton1-754	NBS987	0.710260
Triton1-755	NBS987	0.710257
Triton1-756	NBS987	0.710250
Triton1-758	NBS987	0.710254
Triton1-758	NBS987	0.710253
Triton1-758	NBS987	0.710256
Triton1-758	NBS987	0.710256
Triton1-758	NBS987	0.710258
Triton1-758	NBS987	0.710254
Triton1-758	NBS987	0.710258
Triton1-758	NBS987	0.710262
Triton1-758	NBS987	0.710258
Triton1-758	NBS987	0.710249
Triton1-760	NBS987	0.710255
Triton1-760	NBS987	0.710250
Triton1-760	NBS987	0.710251
Triton1-761	NBS987	0.710248
Triton1-761	NBS987	0.710256
Triton1-761	NBS987	0.710253
Triton1-762	NBS987	0.710252
Triton1-762	NBS987	0.710253
Triton1-763	NBS987	0.710257
Triton1-763	NBS987	0.710249
Triton1-763	NBS987	0.710256
Triton1-768	NBS987	0.710260
Triton1-768	NBS987	0.710257
Triton1-768	NBS987	0.710256
Triton1-768	NBS987	0.710257
Triton1-768	NBS987	0.710253
Triton1-769	NBS987	0.710259
Triton1-769	NBS987	0.710253
Triton1-771	NBS987	0.710250
Triton1-772	NBS987	0.710255
Triton1-772	NBS987	0.710253
Triton1-772	NBS987	0.710254
Triton1-773	NBS987	0.710245
Triton1-773	NBS987	0.710250
Triton1-773	NBS987	0.710248
Triton1-774	NBS987	0.710252
Triton1-774	NBS987	0.710258

Run	BatchText	$^{87}Sr/^{86}Sr$
Triton1-774	NBS987	0.710253
Triton1-775	NBS987	0.710251
Triton1-776	NBS987	0.710251
Triton1-778	NBS987	0.710256
Triton1-778	NBS987	0.710254
Triton1-778	NBS987	0.710253
Triton1-778	NBS987	0.710249
Triton1-780	NBS987	0.710255
Triton1-780	NBS987	0.710258
Triton1-780	NBS987	0.710255
Triton1-781	NBS987	0.710245
Triton1-782	NBS987	0.710251
Triton1-782	NBS987	0.710253
Triton1-782	NBS987	0.710252
Triton1-782	NBS987	0.710247
Triton1-783	NBS987	0.710244
	mean	0.710254
	1SD	0.000005
	2SD	0.00001
	n	146
	%2SD	0.001

Appendix 4. Extra information for chapter 7: Contribution of strontium to the human diet from querns and millstones: an experiment in digestive Sr-isotope uptake.

The experiments contained within this appendix were conducted to compare and validate the Unified Bioaccessibility Method (UBM) employed during the main study in chapter 7, as well as look at smaller, possibly influential components of Sr in the rocks used. The results are approximately on trend with the UBM and are discussed below.

4.1. The Simplified Leach Method

A simplified version of the UBM was conducted in the clean lab at the NIGL (Keyworth, Nottinghamshire). This experiment only represents similar conditions to that of the UBM's upper digestive tract process, not the full digestive tract. The same ground rock samples (<250 μm fraction) were used as in the UBM. Each ground rock sample had 0.2g exposed to 10mL of stomach strength acid HCl (2.5M) in a Savillex© teflon tube at human body temperatures (~37^{o}C) stimulated via the use of a small temperature controlled water bath, for one hour. The end-over-end agitation as seen in the UBM could not be mimicked in the clean lab and instead the samples were shaken approximately every 10 minutes to get similar representation of this process, while trying not to disturb the temperature too much. After one hour the supernant for each sample, termed leach, was collected by centrifuging at 3000rpm for seven minutes and decanting into newly labelled Savillex© teflon beakers. These samples are dried down on a hotplate at 100^{o}C overnight.

The Sr of each sample that underwent the simplified leach method was collected using Dowex AG 50W-X12 resin columns. The Sr of each sample was loaded onto a single Re Filament with TaF following the method of Birck (1986), and the isotope composition and concentrations were determined by Thermal Ionisation Mass spectroscopy (TIMS) using a Thermo Triton multi-collector mass spectrometer. The international standard for $^{87}Sr/^{86}Sr$, NBS987, gave a value of 0.710251 ± .000005 (n=19, 2SD) during the analysis of these samples. Blank values for the clean laboratory were in the region of 100pg.

4.2. Results

The results for the ground samples that underwent the simplified leach method for each rock are in Table 1. The $^{87}Sr/^{86}Sr$ and Sr concentration (ppm) of the ground rock samples that only underwent the UBM upper digestive tract are also displayed in Table 1.

Lithology	**Sample type**	**Sr ppm**	**$^{87}Sr/^{86}Sr$**	**Δsimplified rock flour leach-UBM upper digestive tract.**	**Whole Rock Sr ppm**	**Whole Rock $^{87}Sr/^{86}Sr$**
Millstone Grit	UBM upper digestive tract	3	0.71434	0.0020	106	0.72079
	Simplified Ground Rock Leach	177	0.71632			
Pennant Sandstone	UBM upper digestive tract	4	0.71496	0.0019	57	0.73028
	Simplified Ground Rock Leach	175	0.71683			
Eskdale Granite	UBM upper digestive tract	3	0.73400	0.0226	27	0.91373
	Simplified Ground Rock Leach	102	0.74487			

The upper digestive tract of the UBM was cross referenced with the results of simplified leached method. From the results of the simplified leach method (see sample type Simplified Ground Rock Leach in Table 1), there is an elevated difference of +0.0020 for the Millstone Grit, +0.0019 for the Pennant Sandstone and +0.0226 for the Eskdale Granite when compared to the upper digestive tract of the UBM. There is also a large difference in the Sr concentrations between the simplified leach method and the upper digestive tract of the UBM for each rock type. These elevations in $^{87}Sr/^{86}Sr$ and Sr concentrations (ppm) are understandable considering that the simplified leach method only used 2.5M HCL to represent the stomach acid, while the UBM mimics all the chemical components of the stomach acid which inevitably may have lessened, or even inhibited, the leaching of higher $^{87}Sr/^{86}Sr$ and Sr concentrations from minerals within the rocks. The overall trends are the same though with the Eskdale granite having the highest $^{87}Sr/^{86}Sr$ value, followed by Pennant Sandstone and then Millstone Grit.

In summary, the full digestive tract of the UBM provides the best estimate for the bioaccessible $^{87}Sr/^{86}Sr$ that can be extracted from ingesting rock grit from these lithologies. The simplified leach method used in the clean lab for the ground rock samples have higher values $^{87}Sr/^{86}Sr$ values relative to the upper digestive tract of the UBM that the method was mimicking, but shows a good comparison in which to validate the UBM process.

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Personal Communications

Evans, J.A., *pers.com*:

- Geochemical Survey of Charnwood Forest on the 17/03/14: teaching methods of collecting plant samples and how it is best to avoid plants that have mud-splash which can lead to soil contamination, resulting in a $^{87}Sr/^{86}Sr$ reflective of the mud-splash and not the plant during chemical analysis.
- First trip to the NIGL (BGS, Keyworth, Nottinghamshire) on the 02/06/14: during physical preparation of plant samples Jane Evans commented that a flaky texture is adequate for the chemical preparation for Sr-isotope analysis.
- Plant $^{87}Sr/^{86}Sr$ data on Silurian sedimentary bedrock of Wales near the village of Boughrood, Powys, sample code USK-01, -02, -03, -04, shared via email 15/12/15.
- Communications about Figure 8.2 in chapter 8 by email 05/09/17. Figure 8.2 displays the quantile regression forest predicted concentration map for Rb in shallow soils. Created using the method of Kirkwood *et al*. (2016) by Jane Evans.

Montgomery J., pers.com:

- Discussed the archaeological humans with $^{87}Sr/^{86}Sr$ >0.714 several times during meeting through study period (2013-2017) and how they are often interpreted simplistically as being from the consumption of crops grown on ancient or granitic rocks. First time would have been specfically on the 16/10/13.
- Communications via email on the 25/08/17 about the four Roman cattle, with enamel $^{87}Sr/^{86}Sr$ = 0.71413 - 0.71582 by Montgomery *et al.* (unpublished report). These cattle were unlikely to have originated from the Malvern Hills because the steep terrain is unsuitable for grazing cattle

Figure X. Legend for all the bedrock geology of each of the study areas in this thesis.

Forest of Dean

Bedrock Geology

Rock Unit	
LIAS GROUP - MUDSTONE, SILTSTONE, LIMESTONE AND SANDSTONE	*Li-msls*
TRIASSIC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Tria-mdss*
TRIASSIC ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Tria-scon*
SOUTH WALES UPPER COAL MEASURES FORMATION - MUDSTONE, SILTSTONE, SANDSTONE, COAL, IRONSTONE AND FERR	*Swucm-msci*
DINANTIAN ROCKS (UNDIFFERENTIATED) - LIMESTONE WITH SUBORDINATE SANDSTONE AND ARGILLACEOUS ROCKS	*Dina-lssa*
UPPER DEVONIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Udev-scon*
LOWER DEVONIAN ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Ldev-mdss*
LOWER DEVONIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Ldev-scon*
PRIDOLI ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Prid-mdss*
LUDLOW ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Ludl-mdss*
WENLOCK ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Wen-mdss*
LLANDOVERY ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Ldvy-mdss*
TREMADOC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Trem-mdss*

Kington (the Stanner-Hanter Complex)

Bedrock Geology

Rock Unit	
PRIDOLI ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Prid-mdss*
LUDLOW ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Ludl-mdss*
WENLOCK ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Wen-mdss*
SILURIAN ROCKS (UNDIFFERENTIATED) - LIMESTONE, MUDSTONE AND CALCAREOUS MUDSTONE	*Silu-lmcm*
UNNAMED IGNEOUS INTRUSION, NEOPROTEROZOIC - FELSIC-ROCK	*Uiaz-felsr*
UNNAMED IGNEOUS INTRUSION, NEOPROTEROZOIC - MAFIC IGNEOUS-ROCK	*Uiaz-mfir*
UNNAMED METASEDIMENTARY ROCKS, NEOPROTEROZOIC - MUDSTONE, SANDSTONE AND CONGLOMERATE	*Umsaz-mdsc*

The Lake District

Bedrock Geology

LEX_RCS_I	
TRIASSIC ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Tria-scon*
PERMIAN ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Pund-mdss*
PERMIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Pund-scon*
PENNINE UPPER COAL MEASURES FORMATION - MUDSTONE, SILTSTONE, SANDSTONE, COAL, IRONSTONE AND FERRICRE	*Pucm-msci*
PENNINE MIDDLE COAL MEASURES FORMATION AND SOUTH WALES MIDDLE COAL MEASURES FORMATION (UNDIFFERENTIA	*Psmcm-msci*
WARWICKSHIRE GROUP - SILTSTONE AND SANDSTONE WITH SUBORDINATE MUDSTONE	*Wawk-sisdm*
PENNINE LOWER COAL MEASURES FORMATION AND SOUTH WALES LOWER COAL MEASURES FORMATION (UNDIFFERENTIATE	*Pslcm-msci*
YOREDALE GROUP - LIMESTONE WITH SUBORDINATE SANDSTONE AND ARGILLACEOUS ROCKS	*Yore-lssa*
YOREDALE GROUP - LIMESTONE, SANDSTONE, SILTSTONE AND MUDSTONE	*Yore-lssm*
DINANTIAN ROCKS (UNDIFFERENTIATED) - LIMESTONE WITH SUBORDINATE SANDSTONE AND ARGILLACEOUS ROCKS	*Dina-lssa*
DINANTIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE, LIMESTONE AND ARGILLACEOUS ROCKS	*Dina-slar*
UNNAMED EXTRUSIVE ROCKS, CARBONIFEROUS - MAFIC LAVA	*Uexc-mflava*
UPPER DEVONIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Udev-scon*
UNNAMED IGNEOUS INTRUSION, LATE SILURIAN TO EARLY DEVONIAN - FELSIC-ROCK	*Uisd-felsr*
WENLOCK ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Wen-scon*
SILURIAN ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Silu-mdss*
ASHGILL ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Ashl-mdss*
CARADOC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Cara-mdss*
ORDOVICIAN ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Ord-mdss*
ORDOVICIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Ord-scon*
UNNAMED EXTRUSIVE ROCKS, ORDOVICIAN - FELSIC LAVA	*Uexo-flava*
UNNAMED EXTRUSIVE ROCKS, ORDOVICIAN - FELSIC TUFF	*Uexo-ftuff*
UNNAMED EXTRUSIVE ROCKS, ORDOVICIAN - MAFIC LAVA	*Uexo-mflava*
UNNAMED EXTRUSIVE ROCKS, ORDOVICIAN - MAFIC TUFF	*Uexo-mftuf*
UNNAMED IGNEOUS INTRUSION, ORDOVICIAN TO SILURIAN - FELSIC-ROCK	*Uiios-felsr*
UNNAMED IGNEOUS INTRUSION, ORDOVICIAN TO SILURIAN - MAFIC IGNEOUS-ROCK	*Uiios-mfir*

The Wrekin

Bedrock Geology

Rock Unit	
PERMIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Pund-scon*
PENNINE MIDDLE COAL MEASURES FORMATION AND SOUTH WALES MIDDLE COAL MEASURES FORMATION (UNDIFFERENTIA	*Psmcm-msci*
WARWICKSHIRE GROUP - MUDSTONE, SILTSTONE, SANDSTONE, COAL, IRONSTONE AND FERRICRETE	*Wawk-msci*
WARWICKSHIRE GROUP - SILTSTONE AND SANDSTONE WITH SUBORDINATE MUDSTONE	*Wawk-sisdm*
PENNINE LOWER COAL MEASURES FORMATION AND SOUTH WALES LOWER COAL MEASURES FORMATION (UNDIFFERENTIATE	*Pslcm-msci*
DINANTIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE, LIMESTONE AND ARGILLACEOUS ROCKS	*Dina-slar*
UNNAMED EXTRUSIVE ROCKS, CARBONIFEROUS - MAFIC LAVA	*Uexc-mflava*
LLANDOVERY ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Ldvy-scon*
TREMADOC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Trem-mdss*
LOWER CAMBRIAN ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Lrc-mdss*
UNNAMED EXTRUSIVE ROCKS, NEOPROTEROZOIC - LAVA AND TUFF	*Uexaz-latu*
UNNAMED METAMORPHIC ROCKS, NEOPROTEROZOIC - METALIMESTONE	*Umaz-mlmst*

Burbage common and woods

Bedrock Geology

Rock Unit	
LIAS GROUP - MUDSTONE, SILTSTONE, LIMESTONE AND SANDSTONE	*Li-msls*
TRIASSIC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Tria-mdss*
TRIASSIC ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Tria-scon*
PENNINE MIDDLE COAL MEASURES FORMATION AND SOUTH WALES MIDDLE COAL MEASURES FORMATION (UNDIFFERENTIA	*Psmcm-msci*
WARWICKSHIRE GROUP - MUDSTONE, SILTSTONE, SANDSTONE, COAL, IRONSTONE AND FERRICRETE	*Wawk-msci*
WARWICKSHIRE GROUP - SILTSTONE AND SANDSTONE WITH SUBORDINATE MUDSTONE	*Wawk-sisdm*
PENNINE LOWER COAL MEASURES FORMATION AND SOUTH WALES LOWER COAL MEASURES FORMATION (UNDIFFERENTIATE	*Pslcm-msci*
UPPER CAMBRIAN, INCLUDING TREMADOC - MUDSTONE, SILTSTONE AND SANDSTONE	*Uc-mdss*
MIDDLE CAMBRIAN - MUDSTONE, SILTSTONE AND SANDSTONE	*Mc-mdss*
LOWER CAMBRIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Lrc-scon*
UNNAMED EXTRUSIVE ROCKS, NEOPROTEROZOIC - FELSIC TUFF	*Uexaz-ftuff*

Charnwood Forest

Bedrock Geology

Rock Unit	
TRIASSIC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Tria-mdss*
TRIASSIC ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Tria-scon*
UNNAMED IGNEOUS INTRUSION, ORDOVICIAN TO SILURIAN - FELSIC-ROCK	*Uiios-felsr*
LOWER CAMBRIAN ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Lrc-mdss*
UNNAMED EXTRUSIVE ROCKS, NEOPROTEROZOIC - FELSIC TUFF	*Uexaz-ftuff*
UNNAMED EXTRUSIVE ROCKS, NEOPROTEROZOIC - LAVA AND TUFF	*Uexaz-latu*
UNNAMED IGNEOUS INTRUSION, NEOPROTEROZOIC - MAFIC IGNEOUS-ROCK	*Uiaz-mfir*
UNNAMED METASEDIMENTARY ROCKS, NEOPROTEROZOIC - MUDSTONE, SANDSTONE AND CONGLOMERATE	*Umsaz-mdsc*

The Malvern Hills

Bedrock Geology

Rock Unit	
TRIASSIC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Tria-mdss*
TRIASSIC ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Tria-scon*
PERMIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Pund-scon*
WARWICKSHIRE GROUP - MUDSTONE, SILTSTONE, SANDSTONE, COAL, IRONSTONE AND FERRICRETE	*Wawk-msci*
PRIDOLI ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Prid-mdss*
WENLOCK ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Wen-mdss*
LLANDOVERY ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Ldvy-mdss*
SILURIAN ROCKS (UNDIFFERENTIATED) - LIMESTONE, MUDSTONE AND CALCAREOUS MUDSTONE	*Silu-lmcm*
TREMADOC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Trem-mdss*
UNNAMED EXTRUSIVE ROCKS, NEOPROTEROZOIC - MAFIC LAVA AND MAFIC TUFF	*Uexaz-latm*
UNNAMED IGNEOUS INTRUSION, NEOPROTEROZOIC - FELSIC-ROCK	*Uiaz-felsr*
UNNAMED IGNEOUS INTRUSION, NEOPROTEROZOIC - MAFIC IGNEOUS-ROCK	*Uiaz-mfir*

Nuneaton

Bedrock Geology

Rock Unit	
TRIASSIC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Tria-mdss*
TRIASSIC ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Tria-scon*
PENNINE MIDDLE COAL MEASURES FORMATION AND SOUTH WALES MIDDLE COAL MEASURES FORMATION (UNDIFFERENTIA	*Psmcm-msci*
WARWICKSHIRE GROUP - MUDSTONE, SILTSTONE, SANDSTONE, COAL, IRONSTONE AND FERRICRETE	*Wawk-msci*
WARWICKSHIRE GROUP - SILTSTONE AND SANDSTONE WITH SUBORDINATE MUDSTONE	*Wawk-sisdm*
PENNINE LOWER COAL MEASURES FORMATION AND SOUTH WALES LOWER COAL MEASURES FORMATION (UNDIFFERENTIATE	*Pslcm-msci*
UPPER DEVONIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Udev-scon*
TREMADOC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Trem-mdss*
UPPER CAMBRIAN, INCLUDING TREMADOC - MUDSTONE, SILTSTONE AND SANDSTONE	*Uc-mdss*
MIDDLE CAMBRIAN - MUDSTONE, SILTSTONE AND SANDSTONE	*Mc-mdss*
LOWER CAMBRIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Lrc-scon*
UNNAMED EXTRUSIVE ROCKS, NEOPROTEROZOIC - FELSIC TUFF	*Uexaz-ftuff*

Superficial Geology

Alluvium - Clay, Silt and Sand	
Brickearth - Silt	
Brown Sand - Sand	
Crag Group - Sand and Gravel	
Clay with Flints - Diamicton	
Glacial Sand and Gravel	
Lacustrine Deposits (undifferentiated) - Clay	
Peat	
Raised Marine Deposit (undifferentiated) -Sand and Gravel	
River Terrace Deposit (undifferentiated) - Sand and Gravel	
Sand and Gravel of Uncertain Age and Origin	
Landslip - Unknown Lithology	
Till - Diamicton	
Unknown Lithology - Drift Geology not mapped	

Church Stretton

Bedrock Geology

Rock Unit	
PERMIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Pund-scon*
WARWICKSHIRE GROUP - MUDSTONE, SILTSTONE, SANDSTONE, COAL, IRONSTONE AND FERRICRETE	*Wawk-msci*
WARWICKSHIRE GROUP - SILTSTONE AND SANDSTONE WITH SUBORDINATE MUDSTONE	*Wawk-sisdm*
PRIDOLI ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Prid-mdss*
LUDLOW ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Ludl-mdss*
WENLOCK ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Wen-mdss*
LLANDOVERY ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Ldvy-mdss*
LLANDOVERY ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Ldvy-scon*
SILURIAN ROCKS (UNDIFFERENTIATED) - LIMESTONE, MUDSTONE AND CALCAREOUS MUDSTONE	*Silu-lmcm*
CARADOC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Cara-mdss*
LLANVIRN ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Llvn-mdss*
ARENIG ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Arng-mdss*
TREMADOC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Trem-mdss*
UNNAMED EXTRUSIVE ROCKS, ORDOVICIAN - FELSIC TUFF	*Uexo-ftuff*
UNNAMED EXTRUSIVE ROCKS, ORDOVICIAN - MAFIC TUFF	*Uexo-mftuf*
UNNAMED IGNEOUS INTRUSION, ORDOVICIAN TO SILURIAN - MAFIC IGNEOUS-ROCK	*Uiios-mfir*
LOWER CAMBRIAN ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Lrc-mdss*
UNNAMED EXTRUSIVE ROCKS, NEOPROTEROZOIC - FELSIC LAVA	*Uexaz-flava*
UNNAMED EXTRUSIVE ROCKS, NEOPROTEROZOIC - MAFIC LAVA AND MAFIC TUFF	*Uexaz-latm*
UNNAMED EXTRUSIVE ROCKS, NEOPROTEROZOIC - LAVA AND TUFF	*Uexaz-latu*
UNNAMED IGNEOUS INTRUSION, NEOPROTEROZOIC - FELSIC-ROCK	*Uiaz-felsr*
UNNAMED METASEDIMENTARY ROCKS, NEOPROTEROZOIC - MUDSTONE, SANDSTONE AND CONGLOMERATE	*Umsaz-mdsc*

Cairngorms National Park, Scotland

Bedrock Geology

Rock Unit	
STRATHMORE GROUP - SANDSTONE WITH SUBORDINATE CONGLOMERATE, SILTSTONE AND MUDSTONE	*Seg-scsm*
ARBUTHNOTT-GARVOCK GROUP - SANDSTONE WITH SUBORDINATE CONGLOMERATE, SILTSTONE AND MUDSTONE	*Atgk-scsm*
LOWER OLD RED SANDSTONE - CONGLOMERATE, SANDSTONE, SILTSTONE AND MUDSTONE	*Lors-cssm*
UNNAMED IGNEOUS INTRUSION, LATE SILURIAN TO EARLY DEVONIAN - FELSIC-ROCK	*Uisd-felsr*
UNNAMED IGNEOUS INTRUSION, LATE SILURIAN TO EARLY DEVONIAN - MAFIC IGNEOUS-ROCK	*Uisd-mfir*
UNNAMED EXTRUSIVE ROCKS, SILURIAN TO DEVONIAN - FELSIC LAVA AND FELSIC TUFF	*Uexsd-latf*
UNNAMED EXTRUSIVE ROCKS, SILURIAN TO DEVONIAN - MAFIC LAVA AND MAFIC TUFF	*Uexsd-latm*
UNNAMED IGNEOUS INTRUSION, ORDOVICIAN TO SILURIAN - FELSIC-ROCK	*Uiios-felsr*
UNNAMED IGNEOUS INTRUSION, ORDOVICIAN TO SILURIAN - MAFIC IGNEOUS-ROCK	*Uiios-mfir*
UNNAMED IGNEOUS INTRUSION, ORDOVICIAN TO SILURIAN - ULTRAMAFITITE	*Uiios-umft*
APPIN GROUP - METALIMESTONE	*App-mlmst*
APPIN GROUP - GRAPHITIC PELITE, CALCAREOUS PELITE, CALCSILICATE-ROCK AND PSAMMITE	*App-pgcp*
APPIN GROUP - QUARTZITE	*App-qzite*
ARGYLL GROUP - METALIMESTONE	*Argy-mlmst*
ARGYLL GROUP - PSAMMITE, SEMIPELITE AND PELITE	*Argy-psp*
ARGYLL GROUP - QUARTZITE	*Argy-qzite*
GRAMPIAN GROUP - PSAMMITE AND SEMIPELITE	*Gram-pssp*
GRAMPIAN GROUP - QUARTZITE	*Gram-qzite*
MOINE SUPERGROUP - GNEISSOSE PSAMMITE AND GNEISSOSE SEMIPELITE	*M-gpsp*
MOINE SUPERGROUP - QUARTZITE	*M-qzite*
MOINE SUPERGROUP - SEMIPELITE	*M-sempel*
SOUTHERN HIGHLAND GROUP - LAVA, TUFF, VOLCANICLASTIC ROCK AND SEDIMENTARY ROCK	*Sohi-ltvs*
SOUTHERN HIGHLAND GROUP - PELITE	*Sohi-pel*
SOUTHERN HIGHLAND GROUP - PSAMMITE AND PELITE	*Sohi-pspe*
UNNAMED EXTRUSIVE ROCKS, NEOPROTEROZOIC - MAFIC LAVA AND MAFIC TUFF	*Uexaz-latm*
UNNAMED IGNEOUS INTRUSION, NEOPROTEROZOIC - FELSIC-ROCK	*Uiaz-felsr*
UNNAMED IGNEOUS INTRUSION, NEOPROTEROZOIC - MAFIC IGNEOUS-ROCK	*Uiaz-mfir*

Sherwood Forest

Bedrock Geology

Rock Unit	
TRIASSIC ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Tria-mdss*
TRIASSIC ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Tria-scon*
ZECHSTEIN GROUP - DOLOMITISED LIMESTONE AND DOLOMITE	*Zg-dldo*
PERMIAN ROCKS (UNDIFFERENTIATED) - MUDSTONE, SILTSTONE AND SANDSTONE	*Pund-mdss*
PERMIAN ROCKS (UNDIFFERENTIATED) - SANDSTONE AND CONGLOMERATE, INTERBEDDED	*Pund-scon*
PENNINE UPPER COAL MEASURES FORMATION - MUDSTONE, SILTSTONE, SANDSTONE, COAL, IRONSTONE AND FERRICRE	*Pucm-msci*
PENNINE MIDDLE COAL MEASURES FORMATION AND SOUTH WALES MIDDLE COAL MEASURES FORMATION (UNDIFFERENTIA	*Psmcm-msci*

Dykes Geology

Geological Units	
UNNAMED IGNEOUS INTRUSION, CARBONIFEROUS TO PERMIAN - DOLERITE AND THOLEIITIC BASALT	*Uiicp-dbat*
UNNAMED IGNEOUS INTRUSION, LATE SILURIAN TO EARLY DEVONIAN - FELSIC-ROCK	*Uisd-felsr*
UNNAMED IGNEOUS INTRUSION, LATE SILURIAN TO EARLY DEVONIAN - MAFIC IGNEOUS-ROCK	*Uisd-mfir*
UNNAMED IGNEOUS INTRUSION, ORDOVICIAN TO SILURIAN - MAFIC IGNEOUS-ROCK	*Uiios-mfir*

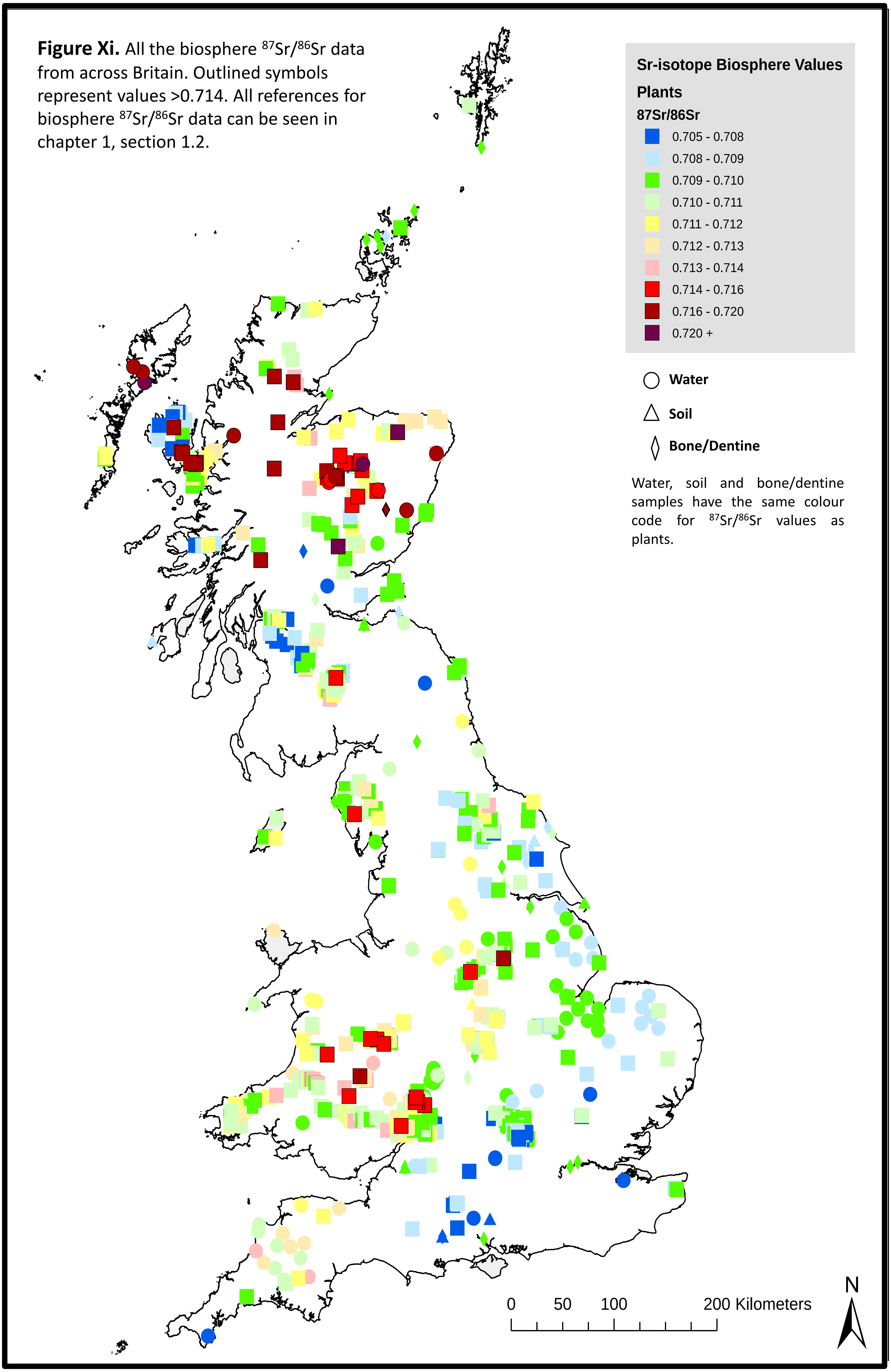

Figure Xi. All the biosphere $^{87}Sr/^{86}Sr$ data from across Britain. Outlined symbols represent values >0.714. All references for biosphere $^{87}Sr/^{86}Sr$ data can be seen in chapter 1, section 1.2.